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LVIII. *The X-ray K-Fluorescence Yield.* By IVOR BACKHURST, M.Sc., *Physics Department, National Physical Laboratory, Teddington, Middlesex* *.

Introduction.

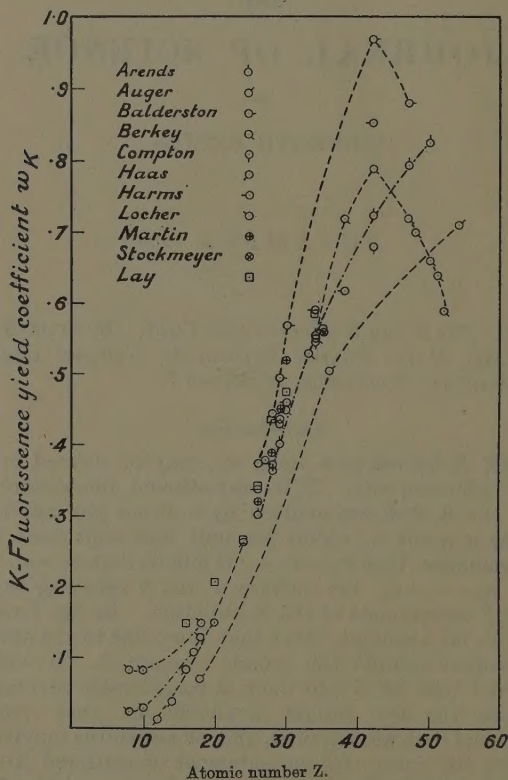
THE K-fluorescence yield, w_K , may be defined in the following way. If, for any element, photo-electrons from the K-shell are emitted by n atoms per unit time, and as a result n_K atoms per unit time emit some type of K radiation, then $w_K = n_K/n$. It follows that $w_K = w_\alpha + w_\beta$, since $n_K = n_\alpha + n_\beta$, the suffixes α and β referring to the α and β components of the K radiation. In fig. 1 values of w_K so far available, other than those due to the author, are plotted against the atomic number Z . It will be observed that for $Z > 40$ there is considerable divergence between the few results available in that region. Additional data are required, and, as apparatus previously used by the author for measurement of scattered X-rays was very suitable for the purpose, w_K has been determined for nine elements between $Z = 42$ and $Z = 56$.

Measurements have not yet been made on elements of higher atomic number than 56, on account of the low absorption, in the type of ionization chamber available,

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of radiation of sufficient hardness to excite the required fluorescent radiation in sufficient quantity. A further reason has been that, if the applied voltage was increased too much, the dimensions of the X-ray tube in use

Fig. 1.



rendered it unserviceable for operation with the degree of steadiness essential to the purpose in hand.

Apparatus and Method of Experiment.

The experimental arrangement and the method of attack were similar to those described in some detail

by the author⁽¹⁾ for the absolute measurement of scattering coefficients of carbon and aluminium, though in the present case no correction for polarization was necessary, the absence of polarization of characteristic radiation having been already established. The primary beam from a self-protected X-ray tube, having a gold anticathode cooled by a forced circulation of oil, passed through an aluminium crystal 3 mm. thick, cut with two plane faces parallel to the same (110) crystal plane. The crystal could be turned so that a beam of the desired wave-length was diffracted from a (111) plane situated perpendicular to the cut faces. This beam, referred to below as the incident beam, fell on the specimen of the element under examination, when the latter was placed at the spectrometer axis.

When possible, as for Mo, Rh, Pd, Ag, Cd, and Sn, the specimens or "radiators" were in the form of flat strips approximately $60 \times 6 \times 1$ mm. in size. A radiator was clamped at one end in the spectrometer chuck and a plane face carefully aligned at an optically determined angle, usually 45° , to the incident beam, in order that absorption corrections might be calculated as accurately as possible. An ionization chamber, carried by the spectrometer arm, could be turned to make an angle $\Phi = 90^\circ$ with the incident beam, a circular lead diaphragm being fitted to the chamber, when in this position, in order to limit the cone of fluorescent rays received to a solid angle of approximately 0.004. The same ionization chamber could be used at $\Phi = 0^\circ$ to receive the incident beam, when the radiator was not in position.

Measurement of the two kinds of radiation thus took place as nearly as possible under the same conditions, since the divergence of the rays was not greatly different in the two cases. The ratio of the ionization currents was obtained by means of a Compton electrometer used as a null instrument in conjunction with a potentiometer and an air-dielectric condenser. In order to bring the ratio to a convenient value, the exposure time of the incident beam was limited to approximately 1/50 sec., or multiples, by means of a sector disk, rotated by a synchronous A.C. motor and used in conjunction with a hand-operated shutter. The exposure time for the fluorescent beam was from 2 to $3\frac{1}{2}$ minutes. A full wave rectification constant potential plant was used to operate

the X-ray tube. Hand control of the filament current of the X-ray tube and of the current to the high potential plant was maintained during observations, a galvanometer being used for the measurement of the main X-ray tube current and an attracted disk voltmeter for the applied potential.

All limiting apertures for the incident beam (other than those merely excluding stray radiation) and for the primary beam from the X-ray tube, together with the aluminium crystal used to obtain the incident beam, were held in position by short rigid mounts clamped to the X-ray tube itself. As a result, any movement of the spectrometer arm carrying the ionization chamber was without influence on the intensity of the incident beam even when, as a test, the counterpoising of the chamber was materially upset. A motion of one or two thousandths of an inch, as checked by a vertical microscope, of the radiator on the spectrometer axis, was found to have no measurable effect on the intensity of the fluorescent rays entering the chamber. The X-ray tube and spectrometer were supported by a stout wooden table standing on a concrete floor, and the X-ray intensity ratios were found to be independent of any relative motion of the apparatus parts that could occur due to normal temperature or humidity changes, vibration or change of position of objects in the room.

On account of absorption in the radiator, the emergent intensity of fluorescent radiation excited at a depth nearly equal to the thickness of the radiator was negligible, *i. e.*, sufficiently thick radiators were in all cases used to secure the maximum intensity of fluorescent radiation. The radiators were also just sufficiently wide to allow the whole of the cone of fluorescent rays entering the ionization chamber to emerge from the radiator face upon which the incident beam fell. For radiators narrower than this the absorption correction would be complicated by the difficulty of ascertaining the proportion of fluorescent radiation emerging from the edge of a radiator, while for wider or thicker radiators the amount of unwanted scattered radiation would be unnecessarily increased.

Since the cone of rays received by the ionization chamber was very narrow, the measured intensity of

K α radiation, under the above conditions, is given by the expression

$$Q_{\alpha} = I_0 \cdot A \cdot \frac{(J_K - 1)}{J_K} \cdot \tau_0 \cdot \lambda_0 \cdot \frac{w_{\alpha} \cdot e^{-\mu_{\alpha}' d'}}{\lambda_{\alpha} (\mu_0 + \mu_{\alpha})} \cdot F_{\alpha} \cdot R_{\alpha},$$

and Q_{β} , the measured intensity of the K β radiation, by a similar expression with suffix β instead of α . The measured intensities of the incident beam Q_0 , unmodified scattered beam Q_u , and modified scattered beam Q_m are given by

$$Q_0 = I_0 \cdot e^{-\mu_0' d'} \cdot F_0 \cdot R_0,$$

$$Q_u = I_0 \cdot A \cdot s_u \cdot e^{-\mu_0' d'} \cdot \frac{(1 - e^{-2\mu_0 \cdot d \cdot \sec \theta})}{2\mu_0} \cdot F_0 \cdot R_0,$$

$$Q_m = I_0 \cdot A \cdot s_m \cdot e^{-\mu_0' d'} \cdot \frac{(1 - e^{-(\mu_0 + \mu_m) d \cdot \sec \theta})}{\mu_0 + \mu_m} \cdot F_m \cdot R_m.$$

In the above expressions,

I_0 = intensity of incident beam;

A = solid angle subtended at radiator by ionization chamber aperture;

θ = semiangle between incident beam and ionization chamber axis;

J_K = ratio of absorption coefficients of radiator at the K absorption edge;

τ_0 = true absorption coefficient in radiator of incident beam.

$\mu_0, \mu_{\alpha}, \mu_{\beta}, \mu_m$ are the total absorption coefficients in the radiator for the incident, K α , K β , and modified scattered rays respectively.

$\mu_0', \mu_{\alpha}', \mu_{\beta}', \mu_m'$ are similar quantities for the aluminium window of the ionization chamber.

d, d' are the thicknesses of the radiator and ionization chamber window respectively.

s_u, s_m are respectively the unmodified and modified scattering coefficients for the radiator.

$F_0, F_{\alpha}, F_{\beta}, F_m$ are respectively the fractions of the incident, K α , K β , and modified scattered rays absorbed in the methyl bromide of the ionization chamber.

$R_0, R_{\alpha}, R_{\beta}, R_m$ are respectively the sensitivities of the ionization chamber to the incident, K α , K β , and modified scattered rays for equal amounts absorbed.

w_α , w_β are the fluorescence yield coefficients for the $K\alpha$ and $K\beta$ rays respectively.

In the case of a compound such as BaO, for example, the expression for Q_α contains the additional multiplying factor m/ρ , where ρ is the density of barium and m is the mass of barium per c.c. present in BaO, while μ_0 and μ_α then refer to total absorption in BaO. Modifications of a similar kind must, of course, be made to the expressions for Q_β , Q_u , and Q_m .

For the ionization chamber sensitivities we have ⁽²⁾

$$R = 1 - 0.85 e^{-\mu_{\text{BrK}} x} \left(\frac{.w \cdot \tau}{\mu} \right)_{\text{Br}} \cdot \frac{\lambda}{\lambda_{\text{BrK}}} - e^{-\mu' x} \cdot \frac{\sigma}{\mu},$$

where w is the fluorescence yield of Br; μ_{BrK} is the absorption coefficient for BrK rays in Br, σ , τ , μ are respectively the scattering, true absorption, and total absorption coefficients in Br for the rays (λ_0 , λ_α , λ_β , or λ_m) entering the chamber; μ' is the absorption coefficient in Br of the rays scattered by the Br in the methyl bromide of the chamber (nearly enough in the present case, $\mu' = \mu$); x is the effective distance from the path of the X-ray beam to the walls of the chamber.

With the ionization chamber at 90° to the incident beam ($\Phi = 90^\circ$), fluorescent and scattered radiation were received together, while in the other position of the chamber ($\Phi = 0^\circ$) only the "incident" beam was received, the radiator then being removed from the path of the beam. In order to receive the whole of the beam, a larger aperture was fitted to the chamber when in the latter position. The quantity determined directly was, therefore, the ratio

$$E = (Q_\alpha + Q_\beta + Q_u + Q_m) / Q_0.$$

To determine w_K it was necessary to know the relation between w_α and w_β , and also to know s_u and s_m , but these quantities were not required accurately. A considerable alteration in the ratio w_α/w_β made little difference to the value of w_K deduced, since the sensitivity of the ionization chamber was not greatly different for the α and β rays. Q_u and Q_m were small in relation to Q_α and Q_β , and, if omitted, altered the value of w_K deduced by no more than 2 or 3 per cent. The ratio w_α/w_β was obtained from data available ⁽³⁾ for the atomic emission ratio of the $K\alpha$ and $K\beta$ intensities, since the latter ratio is equal to $w_\alpha \nu_\alpha / w_\beta \nu_\beta$,

where ν stands for radiation frequency. The apparent irregularities in these data were insufficient to affect appreciably the values of w_K deduced. The scattering coefficients for $\Phi=90^\circ$, s_u , and s_m were obtained by interpolation from previous results ⁽¹⁾ by plotting the atomic structure factor F , of each element, against $(\sin \theta)/\lambda$ and then using the expressions

$$s_u = KF^2 \text{ and } s_m = K \left(Z - \frac{F^2}{Z} \right) (1 + \alpha)^{-3},$$

where $K = (Le^4 \rho) / (2m^2 c^4 W)$, $\alpha = h\nu / mc^2$, Z = atomic number, L = Avogadro's number, ρ = density, W = atomic weight.

TABLE I.

	Mo.	Rh.	Ba(NO ₃) ₂ .
λ (in Å.)	0.328	0.280	0.221
w_β/w_K	0.134	0.129	0.16
μ_0/ρ	16.31	12.50	5.98
μ_a/ρ	20.07	16.43	4.72
$e^{-\mu'_a d'}$	0.7495	0.8299	0.9469
F_0	0.4379	0.2587	0.1276
F_α	0.9937	0.9292	0.4798
R_0	0.8432	0.8344	0.8001
R_α	0.7351	0.7588	0.8264
Q_0	0.35606	0.21039	0.10039
Q_α	2.7515×10^{-5}	2.7661×10^{-5}	2.6494×10^{-5}
E	7.658×10^{-5}	1.2903×10^{-4}	2.7932×10^{-4}

The absorption coefficients of the incident, fluorescent, and modified scattered radiation in the radiator and in the methyl bromide of the ionization chamber were obtained from Jönsson's tables ⁽⁴⁾. The corresponding absorption coefficients for the aluminium window of the ionization chamber were calculated from data given by Allen ⁽⁵⁾, and the wave-length of the incident radiation was deduced from absorption measurements on copper and aluminium using these data. The fraction F_0 of the incident radiation absorbed in the ionization chamber was determined experimentally with the aid of a gold-leaf electroscope, and F_α , F_β , and F_m were calculated from F_0 by using absorption coefficients from Jönsson's tables.

In Table I. some of the factors entering into the calculation of w_K (Table II.) from the experimental ratio E are given to indicate the appreciable variation of some of these quantities over the wave-length range employed. In particular, a fourfold variation occurred in E and a threefold variation in μ_0/ρ . The ratio R_x/R_0 did not differ from unity by more than about 13 per cent., so that a very accurate evaluation of \bar{x} , a somewhat difficult matter, was fortunately unnecessary.

In order to obtain results for Ba, measurements were made on BaO and $\text{Ba}(\text{NO}_3)_2$ powders. A containing cell was necessary for BaO, however, to prevent atmo-

TABLE II.
Experimental Values of $10^3 \cdot w_K$.

	0.328 Å.	0.280 Å.	0.2345 Å.	Averages.
Mo (42)	785	785
Rh (45)	799	803	..	801
Pd (46)	841	828	..	835
Ag (47)	836	839	..	838
Cd (48)	841	850	..	846
Sn (50)	856	841	868	855
Sb (51)	0.221 Å.	862
Te (52)				872
Ba (56)				900

spheric action and $\text{Ba}(\text{NO}_3)_2$ was consequently found preferable, particularly as it was readily obtained in a highly pure state. A compact block of $\text{Ba}(\text{NO}_3)_2$ was prepared by making into a paste with acetone very fine powder, obtained by prolonged grinding, and then pressing the paste into a rectangular brass frame clamped on to a smooth flat brass plate. On evaporation of the acetone, the powder block was sufficiently strong mechanically to remain in the frame when the latter was unclamped from the brass plate. This method of mounting provided a flat face to the powder block flush with one face of the brass frame, and optical reflexion from the latter could be used for angular adjustment. Although the fine grains of the powder were tightly packed, an absorption correction, deduced as above

on the assumption of complete homogeneity of material, was not entirely adequate, owing to the spaces remaining between the particles. The exact correction required being difficult to calculate, an estimate was made as follows:—

Powder blocks of Sb and Te were prepared in exactly the same way as for $\text{Ba}(\text{NO}_3)_2$ and measurements made with these as well as with multicrystalline slabs of the metals. Absorption corrections, calculated as above, were applied in each case to the experimental ratios found. The value of w_K for stick Sb was 1.018 times greater than that obtained for powdered Sb, and the corresponding ratio for Te was 1.024. The mean of these ratios, 1.021, was employed as the additional absorption correction factor required for the $\text{Ba}(\text{NO}_3)_2$ results.

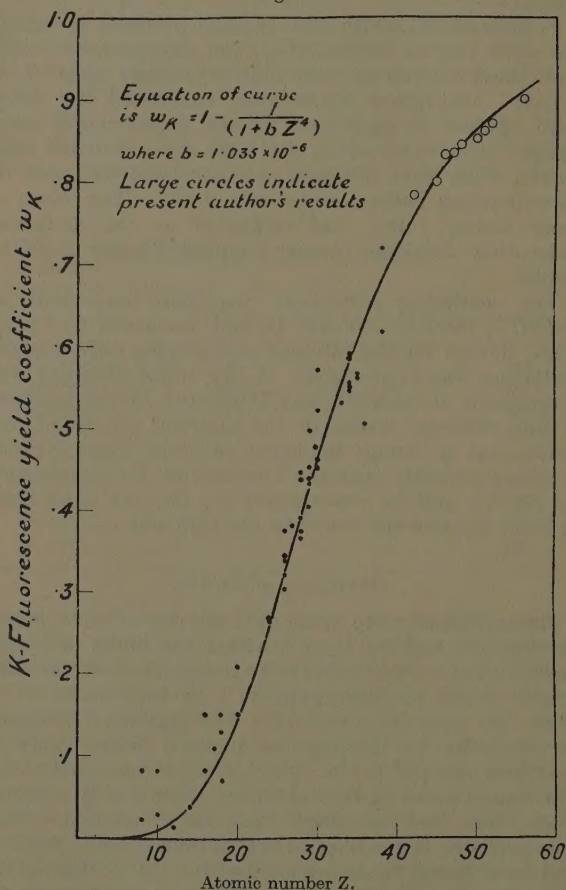
The scattering correction was more important for $\text{Ba}(\text{NO}_3)_2$ than for Sb and Te and amounted to 1.3 per cent., though for the nitrogen and oxygen only modified scattering was appreciable. A low result obtained with a specimen of stick Sb was attributed to the existence of fine cleavage cracks in the material, as Sb of high purity has a strong tendency to form large crystals. It seems probable that the final results for w_K obtained for Sb, Te, and in consequence for Ba, are more likely to be in error on the low than the high side.

Discussion of Results.

Measurements were made at a number of wave-lengths between 0.2 and 0.4 Å., and, within the limits of experimental error, w_K was found to be independent of the wave-length of the incident radiation. In the course of the work the accuracy obtainable was gradually increased, in particular by limiting the incident beam solely by apertures clamped to the X-ray tube, as described above. The values given in the tables are those finally obtained when the best accuracy had been secured. Some unexpectedly low values of w_K obtained with powders, and later found to be occasioned by the powder grains being insufficiently fine, were at first thought to be due to lack of homogeneity of the incident radiation. The possibility of this was carefully examined, though the conclusion reached was that the degree of inhomogeneity

was insufficient to affect the results to an appreciable extent. At 0.328 \AA . the homogeneity of the radiation was examined in the following way :—

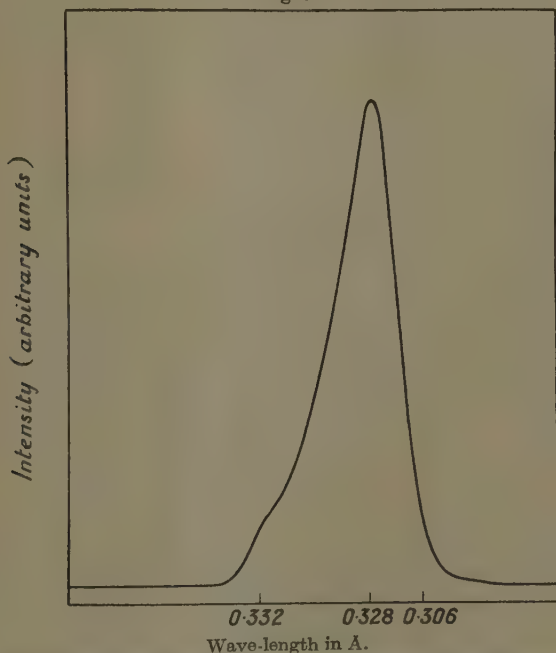
Fig. 2.



An analysis of the incident beam was made, using a calcite crystal in the anti-parallel position with regard to the aluminium crystal, the absorption coefficient of

rays reflected by the calcite being measured at different settings of the latter. When the effective wave-length of the incident beam was 0.328 \AA ., the spectral intensity distribution in the beam was found to be as shown in fig. 3. The effective wave-length was found by measuring the absorption in sheets of 6.263 mm . aluminium and in sheets of 0.322 mm ., 0.212 mm ., and 0.110 mm . of copper,

Fig. 3.



Spectral energy distribution of incident radiation for mean wave-length of 0.328 \AA . Calcite analysing crystal in antiparallel position.

the corresponding wave-lengths deduced being 0.3249 , 0.3285 , 0.3295 , and 0.3285 \AA . respectively, giving the mean wave-length of 0.328 \AA .

According to the theoretical work of Taylor and Burhop ⁽⁶⁾ and of Wentzel ⁽⁷⁾, the internal conversion coefficient $(1-w_K)$ should be approximately proportional to $1/(1+bZ^4)$, where " b " is a constant. The curve of fig. 2 is drawn with $b=1.035 \times 10^{-6}$ chosen to fit

the experimental result for Cd. As shown in Table III., the average difference, neglecting sign, between this curve

TABLE III.

	$10^3 \cdot w_K$. Experi- mental.	$10^3 \cdot w_K$. From curve.	Per cent. differ- ence.	Average per cent. differ- ence.
Mo	785	763	2.9	
Rh	801	809	-1.0	
Pd	835	823	1.5	
Ag	838	835	0.4	
Cd	846	846	0.0	1.2
Sn	855	866	-1.3	
Sb	862	875	-1.5	
Te	872	883	-1.2	
Ba	900	910	-1.1	

TABLE IV.

Z.	$10^3 \cdot w_K$.	Z.	$10^3 \cdot w_K$.	Z.	$10^3 \cdot w_K$.
1....	<0.5	20....	142	39....	705
2....	"	21....	168	40....	726
3....	"	22....	195	41....	745
4....	"	23....	225	42....	763
5....	1	24....	256	43....	780
6....	1	25....	288	44....	795
7....	2	26....	321	45....	809
8....	4	27....	355	46....	823
9....	7	28....	389	47....	835
10....	10	29....	423	48....	846
11....	15	30....	456	49....	856
12....	21	31....	489	50....	866
13....	29	32....	520	51....	875
14....	38	33....	551	52....	883
15....	50	34....	580	53....	891
16....	63	35....	608	54....	898
17....	80	36....	635	55....	904
18....	98	37....	660	56....	910
19....	119	38....	683		

and the author's results is 1.2 per cent. Values of w_K calculated from the equation to the curve are contained in Table IV.

Comparison with Earlier Results.

It will be seen that the curve of fig. 2 agrees fairly well with the results already available for elements of atomic number less than Mo. For Br, w_K from the curve is 0.608. Compton's ⁽²⁾ result for Br of 0.565 has been used in calculating the sensitivity "R" of the ionization chamber, but since this quantity varies only slowly with the wave-length, negligible difference would be made in the results by using the former value for w_K for Br in calculating "R." The agreement of the results obtained by Compton and by Stockmeyer ⁽⁸⁾ for Br and by Compton, Berkey ⁽⁹⁾, and by Arends ⁽¹⁰⁾ for Se suggests that w_K in this region is rather less than that given by the curve of fig. 2, but, as far as present theory goes, there is no actual justification for expecting a curve of this form to give an entirely accurate representation of w_K . According to the calculations recently made by Burhop ⁽¹¹⁾, w_K for Ag should be approximately 0.58 as against 0.835 from the present results. In Burhop's work, however, a number of approximations had to be made, which included the use of hydrogen-like wave-functions and the neglect of the $K\beta$ coefficient, also the treatment was non-relativistic. Harms ⁽¹²⁾ has given his results in a manner in which w_K is not directly tabulated, and w_K has since been deduced from them in different ways. In the method used here w_K has been obtained from the relation

$$w_K = (u_\alpha i_\alpha / i_p) \div (u_\beta i_\beta / i_p) = (u_\alpha i_\alpha / i_p) \{1 + (4\nu_\alpha / 15\nu_\beta)\},$$

where the right-hand expressions are in Harms's notation. For $u_\alpha i_\alpha / i_p$, average values have been taken of those given by Harms for air and carbon dioxide. Harms's results, except for Mo, are then in quite fair agreement with the curve.

In deducing w_K from Balderston's ⁽¹³⁾ results, Jöns-son's ⁽⁴⁾ equation $J_K = E_K / E_L$ has been used, employing energy level values given by Siegbahn ⁽¹⁴⁾. In this connexion it may be remarked that in some of the published tables reproducing the results of Balderston, and also of Martin ⁽¹⁵⁾, there has been confusion between w_K , as defined in this paper, and the quantity $w_K(J_K - 1) / J_K$, which is equal to n_K / n_T , where n_T is the total number of atoms per unit time emitting photo-electrons (K, L, M, etc.) and n_K is the number of atoms, which as a result emit some type of K radiation.

Table V. contains, together with those of the author, the experimental values of w_K that are plotted in fig. 1, except those due to Auger ⁽¹⁶⁾, Stockmeyer and Locher ⁽¹⁷⁾. Stockmeyer found w_K for Br to be 0.56. Locher found

TABLE V.
Experimental Values of $100w_K$.

	Arends.	Lay.	Martin.	Balder- ston.	Ber- key.	Haas.	Harms.
Mg (12)	1.3	..
Si (14)	3.8	..
S (16)	15	8.3	..
Cl (17)	10.8	..
Ca (20)	20.7	15.0	..
Cr (24)	26.5	26.3	..
Fe (26) ...	30.2	34.3	32	37.5	..		33.8
Co (27)	38	Compton.	..
Ni (28) ...	36.4	43.6	39	44.5	39	37.4	..
Cu (29) ...	40.1	..	45	49.5	43	..	43.7
Zn (30) ...	45.0	47.6	52	57	45	..	46.0
As (33)	53
Se (34) ...	55.0	58.5	55	54.7	59.2
Br (35)	56.5	..
Sr (38)	Backhurst.		..	72	..	61.7
Mo (42) ...	72.4		78.5	97	79	68	85.3
Rh (45)		80.1
Pd (46)		83.5
Ag (47) ...	79.5		83.8	88	72
Cd (48)		84.6	..	70
Sn (50) ...	82.5		85.5	..	66
Sb (51)		86.2	..	64
Te (52)		87.2	..	59
Ba (56)		90.0

w_K for oxygen, neon, and argon to be either 0.082, 0.083, and 0.149 respectively, or 0.023, 0.028, and 0.128 respectively, according to the values taken for certain absorption coefficients. Auger's values for w_K for argon, krypton, and xenon were 0.07, 0.505, and 0.71 respectively. The last two authors used the cloud-chamber method to obtain their results. For several elements between $Z=26$ and $Z=42$ a number of determinations of w_K by

ionization intensity measurements are available, as well as the recent photographic intensity measurements by Lay ⁽¹⁸⁾, and, if these are averaged, it is found (Table VI.) that, in spite of the rather wide separation of some of the values, the difference between the average and the curve of fig. 2 does not exceed about 0.04 for any element in this range, even including Mo, for which the separate results for w_K are very scattered. For $Z > 42$ the results recently obtained by Arends are less than those of the author by 0.04 for Ag and 0.03 for Sn, while Balderston's result for Ag is 0.04 greater than that of the author.

TABLE VI.

Z.	Average of experimental results.	w_K from curve of fig. 2.	Difference from curve.	Difference between extreme experimental values.	Number of results averaged.
26 ..	0.336	0.321	0.015	0.073	6
27 ..	0.38	0.355	0.025	..	1
28 ..	0.400	0.389	0.011	0.081	7
29 ..	0.443	0.423	0.020	0.094	6
30 ..	0.488	0.456	0.032	0.120	7
33 ..	0.53	0.551	-0.021	..	1
34 ..	0.565	0.580	-0.015	0.045	6
35 ..	0.563	0.608	-0.045	0.005	2
38 ..	0.669	0.683	-0.014	0.103	3
42 ..	0.800	0.763	0.037	0.290	7

Berkey's results, which show a rapid continuous decrease in w_K as Z increases from 42 to 52, give values for Sb and Te that differ remarkably widely from those found here, and it seems probable that in the incident beam used by Berkey, which consisted mainly of the fluorescent radiation from Ba, there must have been also a band of wavelengths of radiation of softer character. As mentioned above, this would produce an apparent continuous decrease in w_K of the kind observed.

Auger's results are in each case appreciably lower than those given by the curve of fig. 2, while Locher's results are higher. In the region of low atomic number the only values of w_K obtained by ionization intensity measure-

ments are those due to Haas ⁽¹⁹⁾, and these agree well with the curve. Lay's results for $Z=16$ and $Z=20$ are relatively high, but at higher atomic numbers they also agree quite well with the curve of fig. 2.

In conclusion, the author wishes to express his thanks to Dr. G. W. C. Kaye, O.B.E., the Superintendent of the Physics Department, for the continued interest he has taken in this research.

Summary.

The K-fluorescence yield coefficient w_K has been determined for nine elements of atomic number Z between 42 and 56, using apparatus and methods similar to those previously described for the measurement of scattered X-rays (Phil. Mag. xvii. p. 321 (1934)). The results are well represented by $w_K = 1 - 1/(1 + bZ^4)$, where $b = 1.035 \times 10^{-6}$. This corresponds to considerably higher values of w_K than those suggested by recent approximate calculations based on wave-mechanics theory. Comparison is made with results due to other authors, and for $Z < 42$ the average of the results so far available is in reasonably good agreement with the equation given above.

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- (18) Lay, Zeits. f. Phys. xci. p. 533 (1934).
- (19) Haas, Ann. der Phys. xvi. p. 473 (1933).

LIX. *A Note on the Synthesis of Fourier Series.*By A. L. PATTERSON, *M.Sc., Ph.D.**

IN a recent paper J. M. Robertson † describes a very elegant scheme for the computation of double Fourier series, making use of the method originally suggested by C. A. Beevers and H. Lipson ‡. The two-dimensional synthesis is split up into a large number of one-dimensional summations of the type

$$\sum_h A(h) \frac{\cos}{\sin} h(nx_0).$$

Such series are to be summed for N points within the period, x_0 being equal to $360^\circ/N$. Robertson computes a table of $A \cos kx_0$, which he transfers to strips, one for each value of A required. These strips are then mounted in a mechanical sorting device which selects the required values of $A \cos h(nx_0)$ for a given point (nx_0) . These values are added on an adding machine.

Some time ago the writer learned that such a method was in development §, and in particular of its use of the strips, but no details of the sorting device were available. Consequently a sorting method which differs considerably from Robertson's was developed here. As it is somewhat simpler than his, and as it has proved very satisfactory in use, it is thought worth while to describe it briefly.

The strips are prepared as Robertson has described. Those corresponding to positive coefficients are written on white cardboard ($8\frac{1}{2} \times 5/16$ "), another colour being used for the negative coefficients. These strips are mounted on a rack, vertically above one another, in order of their indices h . One of a set of stencils is then set accurately over the rack, so that the openings in it select the correct values of $A \cos h(nx_0)$ for a given point (nx_0) . Certain openings are surrounded by white borders, or are otherwise marked, to indicate that the values read through them are to be given negative signs.

The details of the construction are best left to the reader to adapt to his own requirements. As Robertson

* Communicated by the Author.

† J. M. Robertson, *Phil. Mag.* xxi. p. 176 (1936).

‡ C. A. Beevers and H. Lipson, *Phil. Mag.* xvii. p. 855 (1934).

§ I am indebted to Dr. C. A. Beevers for this information.

has pointed out the value of N chosen should be divisible by four. The same set of strips can then be used for both cosine and sine series, a separate set of stencils being required for each of these types of series. The arrangement of the openings in the stencils can easily be worked out.

Although the writer has not had the opportunity of using Robertson's method, it would seem that the present method would be somewhat faster. In the former the slides carrying the strips have to be reset between each point computed, while in the latter the strips are arranged only once for a given series, the only movement between points being a change of stencils.

Eastman Research Laboratory of Physics,
Massachusetts Institute of Technology,
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February 14th 1936.

LX. *The Numerical Summation of Slowly Convergent Series of Positive Terms.* By W. G. BICKLEY, D.Sc., Imperial College of Science and Technology, and J. C. P. MILLER, Ph.D., University of Liverpool *.

1. Introduction.

MANY problems in pure and applied mathematics lead to infinite series, which must be summed numerically before the solution of the problem can be regarded as complete. Provided the series converge fairly rapidly, so that the desired accuracy can be attained by computing a reasonably small number of terms, no further difficulty arises. When, however, the convergence is slow, some indirect method of summation becomes necessary; several such are known, but in the case of a slowly convergent series of *positive* terms, none of the appropriate methods seem to be applicable unless the n th term is a simple function of n . For series with more complicated terms, we seem to be forced back upon methods which are arithmetical rather than analytical. Arithmetic alone will of course not suffice; we cannot, without some law, "continue"

* Communicated by the Authors.

a series whose early terms are known. In the series which gave rise to the present investigation, for instance, such a "law" was known, but it did not enable the n th term of the series to be calculated independently of its predecessors. Indeed, each term of the series was of the form $C_n f_n(x)$, where the C_n and f_n had to be determined for $n \geq 2$ by means of recurrence formulæ. What could be obtained even here, and analytically, was the ratio of consecutive terms expanded as far as desired in powers of $1/n$, and such an expansion, or at least a few of its leading terms, will usually be obtainable.

In what follows we use such an expansion to determine, for any value of n , a multiplier such that the product of it and the n th term, added to the sum of the first n terms of the series, gives an approximation to the sum of the series considerably better than the partial sum. We also consider certain refinements of the main method, such as a method of successive approximation, as well as a method which achieves the same end by eliminating, rather than determining, the multiplier.

It has become increasingly clear in the course of the work that the case in which the limit of the ratio of successive terms, as n increases indefinitely, is unity, is considerably less complex than when this limit differs from unity. The present paper is almost entirely confined to the former case; some progress with the latter case has been made, and it is hoped to complete the investigation in a future paper.

2.1. We consider a series of positive terms, and denote the r th term by u_r ; we suppose that the series converges to a sum S , *i. e.*,

$$S = \sum_{r=1}^{\infty} u_r; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

further, we denote by S_n the sum of the first n terms, *i. e.*,

$$S_n = \sum_{r=1}^n u_r, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We call the series "slowly convergent" if the ratio $(S - S_n)/u_n$ becomes great compared with unity for moderate values of n . This definition is somewhat loose, but it covers the cases to be dealt with, and the method which seems to be most generally successful consists

essentially in finding a sufficient approximation to this ratio, which we denote by $M(n)$, *i. e.*,

$$M(n) = (S - S_n)/u_n. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We further suppose that it is possible to develop the ratio u_n/u_{n-1} in the form

$$\frac{u_n}{u_{n-1}} = \rho \left\{ 1 - \frac{A_1}{n} + \frac{A_2}{n^2} + \frac{A_3}{n^3} + \dots \right\}, \quad . \quad . \quad (4)$$

in which, if the terms of the series depend upon a variable x (so that S is a function of x), then ρ and the A_r will in general be functions of x ; but not, of course, of n .

The analysis is found to take entirely different forms according as ρ is, or is not, unity; we restrict ourselves for the present to the former case, *i. e.*, when

$$\frac{u_n}{u_{n-1}} = 1 - \frac{A_1}{n} + \sum_{r=2} \frac{A_r}{n^r} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If our series converges, A_1 must be greater than unity. When A_1 is greater than unity, we assume that $M(n)$ can be expressed in the form

$$M(n) = \alpha_{-1}n + \alpha_0 + \frac{\alpha_1}{n} + \frac{\alpha_2}{n^2} + \frac{\alpha_3}{n^3} + \dots \quad . \quad . \quad (6)$$

2.2. Now let

$$S'_n = S_n + M(n)u_n, \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

$$S'_{n-1} = S_{n-1} + M(n-1)u_{n-1}. \quad . \quad , \quad . \quad (7b)$$

If we can determine $M(n)$ so that $S'_n = S'_{n-1}$ for all n , then the common value will be the sum sought. In general this is not accurately possible, but the new sequence S'_n must approach S as a limit, since $M(n)u_n$, which is of the order $\alpha_{-1}nu_n$, approaches zero as a limit, by a condition necessary to ensure the convergence of the original series, ($nu_n \rightarrow 0$).

We may consider S'_n as the partial sum of a new series of terms u'_n , where

$$u'_n = S'_n - S'_{n-1}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and it is evidently possible to determine the α so that u'_n , expanded in powers of $1/n$, vanishes up to any desired power of $1/n$, in which case u'_n will in general be small compared with u_n , and, moreover, the series u'_n will

converge more rapidly than the series u_n , so that S'_n will be a much better approximation to S than is S_n . By (7) and (8)

$$u'_n = u_n \{1 + M(n)\} - u_{n-1} M(n-1). \quad (9)$$

2.3. Now let

$$u'_n = u_{n-1} \sum_{r=0} \beta_r / n^r, \quad (10)$$

when by (5), (6), and (9) we deduce

$$\begin{aligned} \sum_{r=0} \beta_r / n^r &= \{\alpha_{-1}n + (\alpha_0 + 1) + \sum_{r=1} \alpha_r / n^r\} \{1 - A_1/n + \sum_{r=2} A_r / n^r\} \\ &\quad - \{\alpha_{-1}n + (\alpha_0 - \alpha_{-1}) + \sum_{r=1} \alpha_r / (n-1)^r\}. \quad (11) \end{aligned}$$

Expanding the right-hand side (including the last sum) in descending powers of n , and assuming that rearrangement is legitimate, we obtain by equating coefficients of powers of $1/n$

$$\beta_0 = 1 - \alpha_{-1}(A_1 - 1), \quad (12a)$$

$$\beta_1 = \alpha_{-1}A_2 - (\alpha_0 + 1)A_1, \quad (12b)$$

$$\beta_2 = \alpha_{-1}A_3 + (\alpha_0 + 1)A_2 + \alpha_1(A_1 + 1), \quad (12c)$$

$$\dots$$

$$\begin{aligned} \beta_r &= \alpha_{-1}A_{r+1} + (\alpha_0 + 1)A_r + \alpha_1A_{r-1} + \dots - \alpha_{r-1}A_1 + \alpha_r \\ &\quad - (\alpha_1 + {}^{r-1}C_1\alpha_2 + {}^{r-1}C_2\alpha_3 + \dots + \alpha_r). \quad (12r) \end{aligned}$$

We may now choose the α so that $\beta_0, \beta_1, \dots, \beta_r$ all vanish, when we shall have

$$u'_n = u_{n-1} \sum_{s=r+1} \beta_s / n^s, \quad (14)$$

whence it is evident that the series u'_n converges more rapidly than the original series, while its terms can be made as small as we please by taking n sufficiently large, since β_{r+1} is finite; and it is to be expected that these terms will be quite small for a choice of values of n and r not unreasonably large. It cannot, however, be proved that the series $\sum \alpha_r / n^r$ thus formally obtained converges, for it turns out to be definitely asymptotic in certain simple cases (§ 6, *infra*). For fixed n , however, so long as $\alpha_{r+1}/n^{r+1} < \alpha_r/n^r$, we can decrease the u'_n by calculating further terms of $M(n)$.

The rapidity of convergence of the u_n' is easy to determine. If, after choosing the first $(r+1)$ of the α so that $\beta_0, \beta_1, \dots, \beta_r$ all vanish, and assuming the remaining α to be zero, β_{r+s+1} is the first non-vanishing β (s will usually be zero, but the case when it is not will call for remark later), then

$$\begin{aligned}\frac{u_n'}{u_{n-1}'} &= \frac{u_{n-1}}{u_{n-2}} \left(\frac{n-1}{n} \right)^{r+s+1} \frac{\beta_{r+s+1} + \beta_{r+s+2}/n + \dots}{\beta_{r+s+1} + \beta_{r+s+2}/(n+1) + \dots} \\ &= 1 - \frac{A_1 + r + s + 1}{n} + O\left(\frac{1}{n^2}\right), \dots \dots \dots (15)\end{aligned}$$

so that the u_n' converge like $n^{-(A_1+r+s+1)}$, i. e., $(r+s+1)$ stages further along the scale of convergence measured by series whose general term is n^{-p} .

Early values of the α in terms of the A are

$$\alpha_{-1} = 1/(A_1 - 1), \quad \dots \dots \dots (16a)$$

$$\alpha_0 = (A_2 + A_1 - A_1^2)/A_1(A_1 - 1), \quad \dots \dots (16b)$$

$$\alpha_1 = (A_1 A_3 + A_2^2)/(A_1 + 1)A_1(A_1 - 1), \quad \dots (16c)$$

The formulæ become progressively more complicated, but numerical computation is both simple and systematic if the equations $\beta_r = 0$ are solved after substituting the values of the A and of the previously determined α .

3. As an illustration of the efficacy of the foregoing, we apply the process indicated to the series in which $u_r = r^{-2}$. This series converges slowly, but its sum is known to be $\pi^2/6 = 1.64493 \ 40668 \dots$. Here

$$u_n/u_{n-1} = \{n-1\}^2/n^2 = 1 - 2/n + 1/n^2,$$

$$A_1 = 2, \quad A_2 = 1, \quad A_3 = 0 = A_4 = \dots,$$

giving

$$\alpha_{-1} = 1, \quad \alpha_0 = -\frac{1}{2}, \quad \alpha_1 = 1/6, \quad \alpha_2 = 0, \quad \alpha_3 = -1/30, \dots$$

The results are tabulated in columns containing, in order,

$$n, \quad u_n, \quad S_n, \quad S'_n = S_n + nu_n, \quad S''_n = S_n + (n - \frac{1}{2})u_n,$$

$$S'''_n = S_n + (n - \frac{1}{2} + 1/6n)u_n = S_n^{\text{iv}},$$

$$S_n^v = S_n + (n - \frac{1}{2} + 1/6n - 1/30n^3)u_n (= S_n^{\text{vi}}), \text{ and}$$

$$u_n^v = S_n^v - S_{n-1}^v.$$

(The vanishing of α_2 , and as we shall see later, of α_4 , α_6 , . . . , speeds up the approximation; more will be said later upon the possibility of such a "skip" over a power of n^{-1} in $M(n)$.) S_{12}^v is seen to be about 6 units in error in the tenth place, and S_{10}^v about 23 units.

4. It is, in practice, not necessary to perform all the calculations whose results are shown. If results, together with an indication of their accuracy, are all that is required, it would usually be sufficient to calculate a few S_n^v , say for $n=10, 11$, and 12 , when the number of reliable figures would be evident by inspection. If the accuracy proved insufficient, several courses would be open:—

(a) One or more extra terms of the series u_n might be calculated, and the corresponding S_n^v obtained; this is always ultimately successful.

(b) One or more extra α might be calculated and used to find S^v, S^{vi}, \dots ; there may be limits to the accuracy so obtainable, since the series for $M(n)$ may be asymptotic.

(c) The u^v may be made to yield an extra figure or so by a method of successive approximation, involving little labour, next to be outlined.

5.1. We have seen that including terms as far as α_{r-1} in $M(n)$ is equivalent to causing the β to vanish up to and including β_r , so that the $u^{(r)}$ converge (the notation indicating that we have made r of the β vanish) as a first approximation, like $n^{-(A_1+r)}$ —unless there is a "skip" to some greater index. Thus for the $u^{(r)}$, we expect a corresponding $\alpha_{-1}^{(r)}$ equal to $1/(A_1+r-1)$, and the use of the first term of the $M^{(r)}(n)$ will in general effect a further improvement. The idea of proceeding on these lines is attractive on account of its simplicity, and because it can be repeated several times; it suffers, however, from two disadvantages: (i) a "skip" may be overlooked, and (ii) errors in the $u_n^{(r)}$ due to rounding-off, etc., are cumulative. An overlooked "skip" is serious. It will be evident from (12 a) that an incorrect $\alpha_{-1}^{(r)}$ will not annihilate $\beta_n^{(r)}$ so that the index of $1/n$ in the $u^{(r)}$ calculated with this incorrect $\alpha_{-1}^{(r)}$ will be no greater than in $u^{(r)}$, and, moreover, further applications of the same idea will be powerless to effect much improvement

n .	u_n .	S_n .	$S'_n = S_n + nu_n$.	S''_n .	$S'''_n = S''_n \cdot u_n$.	$S^{\text{iv}}_n = S'''_n \cdot u_n$.	$S^{\text{v}}_n = S^{\text{iv}}_n \cdot u_n$.	u_n^{v} .
1	1.0000	0000 0	1.0000 0000 0	2.0000 0000 0	1.50000 00000 0	1.66666 66666 7	1.63333 33333 3	—
2	.25	1.25	1.75	1.625	1.625	1.64583 33333 3	1.64479 16666 7	1145 83333 4
3	.1111 1111 1	1.3611 1111 1	1.69444 4444 4	1.63888 88888 9	1.64506 17284 0	1.64496 52777 8	1.64493 27257 0	13 28875 2
4	.0625	1.42361 1111 1	1.67361 1111 1	1.64236 1111 1	1.64496 52777 8	1.64496 52777 8	1.64493 27257 0	81715 1
5	.04	1.46361 1111 1	1.66361 1111 1	1.64361 1111 1	1.64494 44444 4	1.64494 44444 4	1.64493 37777 8	10520 8
6	.02777 7777 8	1.49138 88888 9	1.65805 55555 6	1.64416 66666 7	1.64493 82716 1	1.64493 82716 1	1.64493 39849 2	2071 4
7	.02040 81632 7	1.51179 70521 6	1.65465 41950 2	1.64445 01133 9	1.64493 60220 4	1.64493 60220 4	1.64493 40387 4	538 2
8	.01562 5	1.52742 20521 6	1.65242 20521 6	1.64460 95521 6	1.64493 50729 9	1.64493 50729 9	1.64493 40557 4	170 0
9	.01234 56790 1	1.53976 77311 7	1.65087 88422 8	1.64470 60027 7	1.64493 46264 6	1.64493 46264 6	1.64493 40619 6	62 2
10	.01	1.54976 77311 7	1.64976 77311 7	1.64476 77311 7	1.64493 43978 4	1.64493 43978 4	1.64493 40645 1	25 5
11	.00826 44628 1	1.55803 21939 8	1.64894 12848 9	1.64480 90534 9	1.64493 42726 2	1.64493 42726 2	1.64493 40656 5	11 4
12	.00694 44444 4	1.56497 66384 2	1.64830 99717 5	1.64483 77495 3	1.64493 42001 5	1.64493 42001 5	1.64493 40661 9	5 4

since they too will not remove this lowest power of $1/n$. It is therefore essential to test the possibility of a "skip." Analytically this means testing whether $\alpha_r=0$, along with the values of the preceding α , satisfies $\beta_{r+1}=0$, and if this entails little labour, then the determination of a (non-zero) value of α_r , and the consequent addition of a term to $M(n)$, almost certainly entails very little more. It will, indeed, only be when improvements in $M(n)$ are laborious that the comparative simplicity of this method will outweigh its disadvantages, and we must then fall back upon an empirical test. The simplest test is to plot $\log u_n^{(r)}$ against $\log n$. This is done in the figure for our sample series, using the u^v , and the lines whose slope corresponds to the indices 7 (as expected) and 8 are there drawn. It is seen that 8 is a better fit than 7, so that a better approximation will be obtained by adding $nu_n^{(r)}/7$. The improvement is definite, but the results are still in error in the tenth place. With regard to cumulative error, should there be a possible error of δ in any $u^{(r)}$, there will be a possible error of $n\alpha_{-1}^{(r)}\delta$ in $S_n^{(r)}$ and thus an error not exceeding $(2n-1)\alpha_{-1}^{(r)}\delta$ in $u_n^{(r)'}; consequently a possible error of $(2n-1)^2\alpha_{-1}^{(r)}\alpha_{-1}^{(r)'}\delta$ in $u_n^{(r)''}$, and so on.$

5.2. In view of what has just been said, we are tempted to explore the possibilities of obtaining empirically two or more terms of the expansion of $M^{(r)}(n)$. It is not difficult to find constants $A_1^{(r)}$ and $A_2^{(r)}$, which give the best fit to

$$\frac{u_n^{(r)}}{u_{n-1}^{(r)}} = 1 - \frac{A_1^{(r)}}{n} + \frac{A_2^{(r)}}{n^2} + \dots \quad (17)$$

Since $A_1^{(r)}$ must be $A_1 + \text{an integer}$, we have some check upon the satisfactory nature of the result, and an indication of the presence of "skip" if the integer is greater than r .

Using the last four lines of our example, we have an approximation

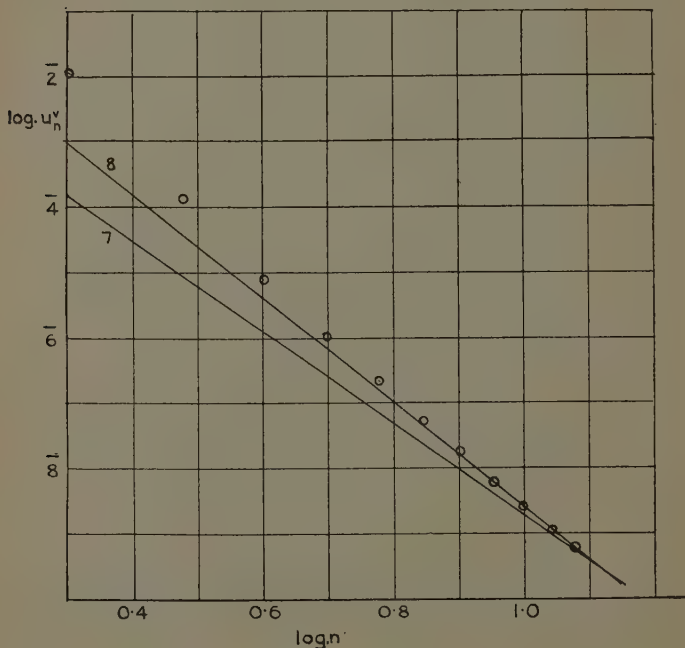
$$\alpha_{-1}^v = 1/7, \quad \alpha_0^v = -5/8,$$

giving, for $n = 12$,

$$S \doteq 1.64493 \ 40667_8,$$

i. e., we have a result correct to 10 places. This is shown, independently of our knowledge of the correct result,

by the values corresponding to $n=11$ and 10 , which end $\dots 67_3$ and $\dots 65_6$ respectively. At the same time, the "dummy" figures in the eleventh place are quite unreliable—a fact which shows up strongly in the calculations leading to the values of α_{-1}^v and α_0^v —so that it is useless to attempt more here, *i. e.*, without computing more figures in the u_n . In any case, indeed,



it is safe to use this last empirical method only as the last stage, for although the corresponding $\alpha_{-1}^{(r)}$ is (almost certainly) exact, $\alpha_0^{(r)}$ as so determined cannot pretend to be so.

As a matter of fact, however, use of the series for $M(n)$ up to the term in α_{13} gives, when $n=10$, results correct to 15 places, and the smallest term of $M(10)$ has not then been reached.

6. For the series of our example the coefficients are Bernoulli numbers, and

$$M(n) = n - \frac{1}{2} + \sum \frac{(-)^r B_r}{n^{2r-1}} \quad . \quad . \quad . \quad (18)$$

(taking $B_1=1/6$, $B_2=1/30$, ... as in 'Calculus of Observations,' by Whittaker and Robinson). This is definitely an asymptotic expansion.

More generally, for $\zeta(s) = \sum 1/n^s$, our treatment gives the known expansion

$$\zeta(s) = \sum_1^n r^{-s} + M(n)n^{-s},$$

where

$$M(n) = \frac{n}{s-1} - \frac{1}{2} + \sum_{r=1} \frac{s(s+1) \dots (s+2r-2)}{2r!} \frac{(-)^r B_r}{n^{2r-1}}.$$

Although $M(n)$ in these examples is asymptotic, it is possible to construct cases in which $M(n)$ is convergent, *e. g.*,

$$\frac{u_n}{u_{n-1}} = \frac{(n-1)^5}{\{n^3 + (n-1)^2\}(n-2)^2} = 1 - \frac{2}{n} + \frac{6}{n^2} - \frac{9}{n^3} + \dots,$$

which gives

$$M(n) = n + 2 + \frac{3}{n} + \frac{4}{n^2} + \dots = \frac{n^3}{(n-1)^2}.$$

A few further remarks about the series (18) may be of interest. It is easily shown to be the asymptotic expansion of

$$n^2 \frac{d^2}{dn^2} \{\log \Gamma(n+1)\},$$

and this form satisfies (8) with $u'_n = 0$, for

$$\begin{aligned} u_n \{1 + M(n)\} &= \frac{1}{n^2} \left[n^2 \frac{d^2}{dn^2} \{\log \Gamma(n+1)\} + 1 \right] \\ &= \frac{1}{n^2} \left[n^2 \left\{ \frac{d^2}{dn^2} \log \Gamma(n) - \frac{1}{n^2} \right\} + 1 \right] \\ &= \frac{d^2}{dn^2} \{\log \Gamma(n)\} \\ &= u_{n-1} M(n-1). \end{aligned}$$

We also have, from (18), the asymptotic expansion,

$$\sum_1^n r^{-2} \sim \pi^2/6 - n^{-2} \left\{ n - \frac{1}{2} + \sum_{r=1} (-1)^r B_r / n^{2r-1} \right\}.$$

7. In addition to the methods outlined above, there is another which has several advantages in practice, the main being that it is entirely computational and can be applied without any recourse to analysis. It consists essentially in the *elimination*, rather than the *determination*, of the α , and leads to a simple equation for the determination of the approximation to S . Since the α are eliminated, there is no danger to be feared from an overlooked "skip," so that the method can be applied two or more times in succession—with a corresponding increase in possible error, of course.

Writing (3) and (6) in the form

$$\frac{S - S_n}{u_n} = \alpha_{-1}n + \alpha_0 + \frac{\alpha_1}{n} + \dots + \frac{\alpha_r}{n^r} + \dots,$$

we multiply through by n^r and obtain

$$\frac{n^r(S - S_n)}{u_n} = \alpha_{-1}n^{r+1} + \alpha_0n^r + \dots + \alpha_r + O(1/n). \quad (19)$$

Taking the $(r+2)$ th difference of this annihilates the terms on the right-hand side up to and including α_r , and assuming that the rest are negligible, we deduce that

$$S \Delta^{r+2} \{n^r/u_n\} = \Delta^{r+2} \{n^r S_n/u_n\}, \quad \dots \quad (20)$$

whence S is determined. Taking the example already used, $\sum n^{-2}$, using $r=2$, we find from the last three pairs of fourth differences

$$\begin{array}{ccc} 99 & & \\ S \doteq 1.64493 & 460, & \\ 37 & & \end{array}$$

actually slightly better than the S_n'' for $u=8, 9$, and 10 respectively.

8. This method is capable of some refinement if numbers ξ_1, ξ_2, \dots can be found such that $M(n)$ takes the form

$$\begin{aligned} \alpha_{-1}n + \alpha_0 + \frac{\gamma_1}{n + \xi_1} + \frac{\gamma_2}{n + \xi_2} + \dots + \frac{\gamma_r}{n + \xi_r} + \sum_{p=1}^{\infty} \frac{\alpha'_{2r+p}}{n^{2r+p}} \\ = \alpha_{-1}n + \alpha_0 + \sum \left(\frac{\alpha_r}{n^r} \right), \quad (21) \end{aligned}$$

Eliminating the p from this set of equations, we finally find that $F_s(n)$ is a constant multiple of

$$\begin{vmatrix} \alpha_{s+1}, & \alpha_s, & \alpha_{s-1}, & \dots & \alpha_2, & \alpha_1 \\ \alpha_{s+2}, & \alpha_{s+1}, & \alpha_s, & \dots & \alpha_3, & \alpha_2 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \alpha_{2s}, & \alpha_{2s-1}, & \alpha_{2s-2}, & \dots & \alpha_{s+1}, & \alpha_s \\ n^s, & n^{s-1}, & n^{s-2}, & \dots & n, & 1. \end{vmatrix} \quad . \quad . \quad (26)$$

It appears that the determination of the optimum $F_s(n)$ demands the knowledge of the α up to α_{2s} , and if these are found it is usually simpler to apply $M(n)$ directly. Thus the main use of the difference method is in cases where the α are difficult to find, and then it is not easy to give a rule which will lead to a multiplier definitely better than n^s . (Better results may be given with, say, $(n+1)^s$.) In one case, however, $s=0$, there is no multiplier, and we can use successive approximation here with no fear of unnecessary lack of convergence.

9. The converse problem, that of series corresponding to special forms of $M(n)$, is of some interest.

If α_{-1} vanishes, A_1 becomes (apparently) infinite. The cause of this is the incorrect assumption that the leading term in the expansion of u_n/u_{n-1} is unity. In general, if we assume

$$M(n) = \alpha_r/n^r + \alpha_{r+1}/n^{r+1} + \dots, \quad . \quad . \quad . \quad (27)$$

we find from (9), with $u_n^s = 0$,

$$\frac{u_n}{u_{n-1}} = \frac{\alpha_r}{n^r} + \frac{r\alpha_r + \alpha_{r+1}}{n^{r+1}} + \dots, \quad (r \geq 2). \quad (28a)$$

For $r=0$,

$$\frac{u_n}{u_{n-1}} = \frac{\alpha_0}{\alpha_0 + 1} + O(1/n), \quad . \quad . \quad . \quad (28b)$$

$r=1$,

$$\frac{u_n}{u_{n-1}} = \frac{\alpha_1}{n} + O(1/n^2), \quad . \quad . \quad . \quad (28c)$$

so that $r=0$ corresponds to series which are, in the long run, mainly geometric, and $r=1$ to series of exponential type.

10. In conclusion, we add a few remarks upon the difficulties encountered with series in which the

$\rho (= \lim u_n/u_{n-1})$ of (4) is less than unity, *i. e.*, of series which ultimately are approximately geometric. In such cases, so long as n has small or moderate values, the diminution of successive terms is caused as much, or more, by the co-factor of ρ in (4) as by ρ itself, and the nearer the value of ρ is to unity the greater must n be made before the effect of ρ becomes dominant. A formal development for $M(n)$ on the lines of this paper commences with the term $\alpha_0 = \rho/(1-\rho)$, and succeeding terms contain the square and higher powers of $\{\rho/(1-\rho)\}$. Thus it is only by taking n prohibitively great—considerably greater than $\rho/(1-\rho)$ —that the series for $M(n)$ becomes manageable. If we notice that the value of α_0 just given is that appropriate to a geometric series of ratio ρ , the failure is explained in the light of the foregoing remarks, in that this value of α_0 takes no account of the co-factor of ρ in (4). An investigation of this case is proceeding, with some success, and we hope to return to it in due course.

LXI. *A Generalization of Schwarzschild's Internal Solution.*

By V. V. NARLIKAR, *Benares Hindu University, India* *.

SCHWARZSCHILD has already obtained the field of a fluid sphere, static and homogeneous. We proceed to obtain here a generalization of it as given by the line-element

$$ds^2 = -R^2[d\chi^2 + \sin^2\chi(d\theta^2 + \sin^2\theta d\phi^2)] + S^2 dt^2, \quad (1)$$

where $R=R(t)$ and $S=S(\chi)$. The familiar cases in which R or S is constant will be excluded from consideration. For a perfect fluid

$$T^\nu_\mu = (\rho + p)g_{\mu\sigma} v^\sigma v^\nu - pg^\nu_\mu \quad . \quad . \quad . \quad (2)$$

in the usual notation. The non-zero components of the energy-momentum tensor are given by the following :

$$-8\pi T_1^1 = -\frac{1}{R^2} + \frac{2S' \cot \chi}{SR^2} - \frac{2R\ddot{R} + \dot{R}^2}{S^2R^2} \quad . \quad . \quad . \quad (3)$$

$$-8\pi T_2^2 = -8\pi T_3^3 = \frac{S''}{SR^2} + \frac{S' \cot \chi}{SR^2} - \frac{1}{R^2} - \frac{2R\ddot{R} + \dot{R}^2}{S^2R^2} \quad (4)$$

* Communicated by the Author.

LXII. *An Experimental Investigation on the Influence of the Polished Surface on the Optical Constants of Copper as determined by the Method of Drude.* By H. LOWERY, Ph.D., D.Sc., F.Inst.P., Principal, North-Western Polytechnic, London, H. WILKINSON, B.Sc., M.Sc.Tech., and D. L. SMARE, B.Sc., Technological Research Scholar, College of Technology, Manchester*.

I. INTRODUCTION.

IN a previous publication ⁽¹⁾ it has been pointed out that one of the principal difficulties in determining the optical constants of metals by katoptric methods is the preparation of suitable reflecting surfaces. Stained or tarnished surfaces or surfaces contaminated by polishing material are useless. Apart from such imperfections, large variations in the values of the refractive index (n), absorption coefficient (K), and reflecting power (R) appear to be due to scratched or matt surfaces—that is, surfaces which have not been completely covered by the Beilby layer—and to the variable thicknesses of the layer produced by different polishing methods.

It is generally agreed ⁽²⁾ that the greater part of the available data indicates that incompletely polished or matt surfaces give reduced values of n and K , and that heavily-flowed or burnished surfaces increase these values. The degree of flow, whilst varying with the polishing technique adopted, is subject to almost uncontrollable variations in the hands of a single operator, so that the foregoing rather indefinite conclusions are of little use to the experimenter. They are conclusions based only on methods of polishing, which, although widely different, are all mechanical and essentially similar inasmuch as they produce a Beilby layer. They leave us with no satisfactory solution to the problem of finding what correction might be applied to optical constants in order to obtain values characteristic of the metal beneath the surface layer. Optical constants which can be regarded as truly characteristic of a metal are of great interest to the theoretical physicist, and it was with the idea of obtaining such optical data that

* Communicated by the Authors.

the experimental work mentioned in this paper was undertaken. Three interesting points arose :—

(i.) Hitherto, surfaces for optical examination have been prepared by mechanical methods of polishing, except in those cases where the cleavage surfaces of single crystals or mercury and molten metals have been used. Recently, however, P. Jacquet ⁽³⁾ has developed an electrolytic method of polishing copper, by means of which a brilliant surface, free from scratches, is produced. This surface is of particular interest, as it has no Beilby layer.

Messrs. Metropolitan-Vickers Electrical Company have also developed in their research laboratories a method of preparing metallic mirrors by the evaporation of thin films of metal on smooth glass surfaces *in vacuo*. A comparison of the dispersion curves of copper, determined for a surface prepared by the usual mechanical methods of polishing and for each of these new types of surface, does give more definite information concerning the effects of surface layers than has previously been obtained.

(ii.) The experimental determination of the dispersion curve of a specimen for the range of wave-lengths used (λ 6800 Å. to λ 4358 Å.) extends over a period of five to seven hours after the completion of polishing. On attempting to make, by way of confirmation, repeated determinations of dispersion curves for an electrolytically polished specimen of copper, variations greater than those due to instrumental experimental error were found. These were first attributed to the deterioration of the mirror on exposure to the atmosphere. The repeat determinations were not always carried out for the full number of wave-lengths previously used, so that the times of exposure after polishing were different. G. P. Thomson ⁽⁴⁾ has shown that copper tarnishes rapidly in air. For example, he obtained electron diffraction patterns, characteristic of copper oxide, from a surface of copper which had been exposed for three-quarters of an hour only. The effect of this tarnishing upon the two quantities measured in the present method, viz. Δ , the phase-difference between the components of the reflected elliptically polarized light, and 2ψ , the azimuth of polarization of the reflected light after it has been restored to plane polarization, and the consequent effect upon n and K , have been studied previously

by Lowery and Moore ⁽⁵⁾. They found that for copper 2ψ was hardly affected, while Δ decreased uniformly with time of exposure. Their curve extended to a time of about 30 hours, and was approximately a straight line.

It was felt, however, that this result was not entirely conclusive, for two reasons: first, it was determined before the Soleil modification of the Babinet compensator had been adopted, the readings with a simple Babinet compensator being less accurate than the present arrangement permits; secondly, it is very probable that such a decay curve should become asymptotic to the time axis. With the more accurate means of measuring Δ now in use the previous investigation has therefore been repeated with results as given below.

(iii.) The time corrections obtained from these redetermined decay curves were, however, still insufficient to explain the variations mentioned above in dispersion curves for electrolytically polished copper. It will be seen from the account given below that the electrolytic polishing method requires that the copper surface shall be initially smooth. To obtain smooth surfaces the specimens were first mechanically polished by the usual metallurgical method, were consequently cold-worked to some extent, and hence possessed the Beilby layer.

It seemed probable that variations in the measured constants might result from the different thicknesses of this disturbed surface removed by the electrolytic polishing process. A series of experiments was accordingly carried out to investigate the dependence of Δ and 2ψ upon the duration of electrolytic polishing.

II. EXPERIMENTAL.

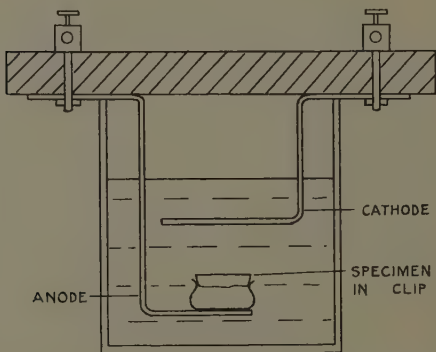
1. General Procedure.

The apparatus and method of measurement were the same as those previously described ⁽¹⁾. A mercury arc and an automatically fed carbon arc were used as sources of light, and a Hilger spectrometer selected a band of light about 20 Å. in width from the continuous spectrum of the arc.

Two pieces of cast copper were used as specimens. These were prepared by melting cleaned electrolytic copper *in vacuo* in a small electric laboratory furnace. The vacuum was maintained overnight as the melt

slowly cooled. Suitable pieces with a surface area of about one square inch were cut from this piece to avoid contraction cavities. These were filed flat and ground to 000 or 0000 emery. At this stage the specimens were annealed *in vacuo* for an hour at 700° C. and cooled slowly over night to remove cold work due to sawing and filing. The specimens remained quite clean and bright, and required no further treatment other than a very light rub on 0000 emery before polishing with magnesia on a wet rotating pad. Unidirectional scratches were avoided by rotating the specimen during the polishing process. The surfaces were rinsed under the tap for a few minutes and then in distilled water. This

Fig. 1.



was allowed to drain from the surface with the specimen propped against a pin, driven through clean filter-paper into the bench, and when almost dry a little absolute alcohol was poured over the specimen several times. Contact with the hand was avoided during these final stages to avoid any contamination of the surface by grease.

2. *Electrolytic Polishing.*

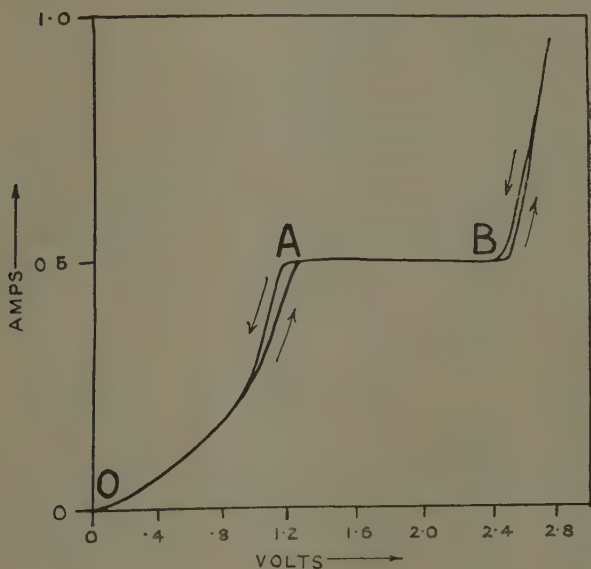
This process was carried out on the same specimens which had undergone a preliminary process of mechanical polishing as described above.

The phenomenon of electrolytic polishing occurs under particular conditions of current and voltage in a cell

containing a solution of orthophosphoric acid (sp. gr. 1.3–1.4). The copper to be polished was made the *anode*, and a copper sheet about 8×6 cm. was used as the cathode. A spring clip held the specimens firmly and formed the electrical contact (fig. 1).

As the current through the cell is increased, voltage and current rise together, following the smooth curve OA (fig. 2) (obtained during preliminary trials). At the

Fig. 2.



point A (1.2–1.4 volts) the voltage jumps violently to a value corresponding to the point B (2.0–2.4 volts), while the current tends to drop unless maintained steady at about 0.5 amps. by means of a sliding resistance. At voltages greater than B oxygen is evolved at the anode, and current and voltage again rise together. The polishing occurs under conditions represented by the flat portion of the curve AB.

Good results were obtained with a potential of 1.95 to 2.00 volts and a current of about 0.65–0.75 amp.

passing through the cell; the separation of the electrodes was within 1 mm. of 2.2 cm. in all cases. These conditions corresponded to a point near B. In order to avoid etching the anode, which occurs at voltages below point A, the current was increased very rapidly until the jump in voltage occurred, care being taken that this jump did not exceed 2 volts, to avoid bubbles of oxygen forming on the anode surface. After this the voltage was adjusted to 1.95–2.00 volts as soon as possible. Some time was required before conditions became steady. At this stage the current was usually decreasing and the voltage increasing very slowly.

A black film appears on the anode surface during the time of preliminary adjustment of current and voltage. This disappears slowly and governs the time of polishing. The film washes off readily, but leaves an imperfectly polished surface marred by milky-white lines in a dendritic pattern, probably based on the crystalline structure of the copper crystals beneath. The more rapidly the voltage is adjusted the less dense is the black film and the more rapid is its disappearance, though a perfect polish is hardly possible in less than 5 minutes. The same procedure of washing and drying was followed as with the mechanically polished surfaces.

Jacquet has shown the absence of any amorphous Beilby layer on copper polished this way by electrodepositing copper on both mechanically polished and electrolytically polished surfaces. The crystals of deposited copper built up a continuation of the crystalline arrangement already existing in the case of the electropolished surface, whereas the new crystals were formed with no predetermined pattern on top of the amorphous Beilby layer.

3. *The Evaporated Mirrors.*

These were made by evaporating the metal on to a clean surface of good quality glass under conditions of evacuation such that the mean free path of the metal atoms is of the same order as the dimensions of the evaporating chamber. The film of metal formed is perfectly smooth and is of sufficient thickness to ensure maximum reflexion of incident light.

Electron diffraction experiments on evaporated films

of metal have shown the film to be of crystalline structure, though the crystals are probably extremely minute.

Small sections about 1" wide were cut from these mirrors and used for the purpose of measurement.

Specimens were prepared late in the day (at the works of Messrs. Metropolitan-Vickers Electrical Company), left under vacuum in the evaporating chamber overnight, removed next morning, cut and carried to the laboratory in a vacuum desiccator containing fresh calcium chloride. The optical constants were measured on the same day. Two independently prepared specimens were used.

TABLE I.

Effect of Exposure on Δ and 2ψ .

Specimen A. $\theta=70^\circ$ throughout. $\lambda=6400 \text{ \AA.}$ and 5400 \AA.

Time interval between cessation of electro- lytic polishing and mean time of measure- ment of constants.	$\lambda=6400 \text{ \AA. (H. W.).}$		$\lambda=5400 \text{ \AA. (D. L. S.).}$	
	Δ .	2ψ .	Δ .	2ψ .
hr. min.				
0 00.....	$103^\circ 27'*$	—	$89^\circ 0'*$	—
0 51.....	$103^\circ 6'$	$88^\circ 1'$	—	—
1 02.....	—	—	$88^\circ 26'$	$74^\circ 30'$
2 16.....	$101^\circ 54'$	$87^\circ 57'$	—	—
2 32.....	—	—	$86^\circ 50'$	$73^\circ 54'$
3 33.....	$101^\circ 36'$	$87^\circ 51'$	—	—
3 52.....	—	—	$86^\circ 42'$	$74^\circ 9'$
5 36.....	$101^\circ 24'$	$87^\circ 50'$	—	—
5 55.....	—	—	$85^\circ 59'$	$74^\circ 41'$
7 46.....	$100^\circ 42'$	$87^\circ 56'$	—	—
8 11.....	—	—	$85^\circ 44'$	$74^\circ 39'$
9 54.....	$100^\circ 0'$	$87^\circ 49'$	—	—
10 22.....	—	—	$85^\circ 16'$	$74^\circ 37'$
12 24.....	$99^\circ 56'$	$87^\circ 52'$	—	—
12 44.....	—	—	$84^\circ 59'$	$74^\circ 33'$
15 47.....	—	—	$84^\circ 55'$	$74^\circ 41'$
16 03.....	$99^\circ 42'$	$87^\circ 50'$	—	—
24 52.....	$99^\circ 28'$	$87^\circ 56'$	—	—
25 18.....	—	—	$84^\circ 59'$	$74^\circ 44'$
29 27.....	$99^\circ 28'$	$88^\circ 0'$	—	—
29 41.....	—	—	$84^\circ 59'$	$75^\circ 1'$

* By extrapolation.

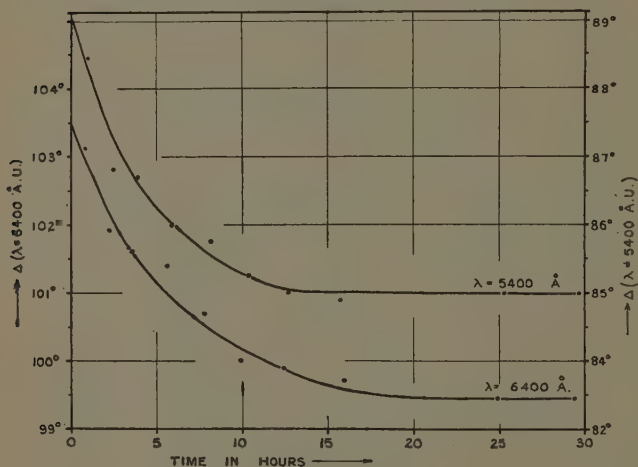
4. *The Effect of Exposure.*

Specimen A of cast copper prepared and electrolytically polished for 12 minutes, as described above, was used

in this investigation. Using an angle of incidence of 70° , which remained unaltered throughout the experiment, the values of Δ and 2ψ were determined by two observers for wave-lengths 6400 \AA. (observer H. W.) and 5400 \AA. (observer D. L. S.) alternately over a period of 30 hours.

The results are summarized in Table I. and the decay curves are plotted in fig. 3.

F g. 3.



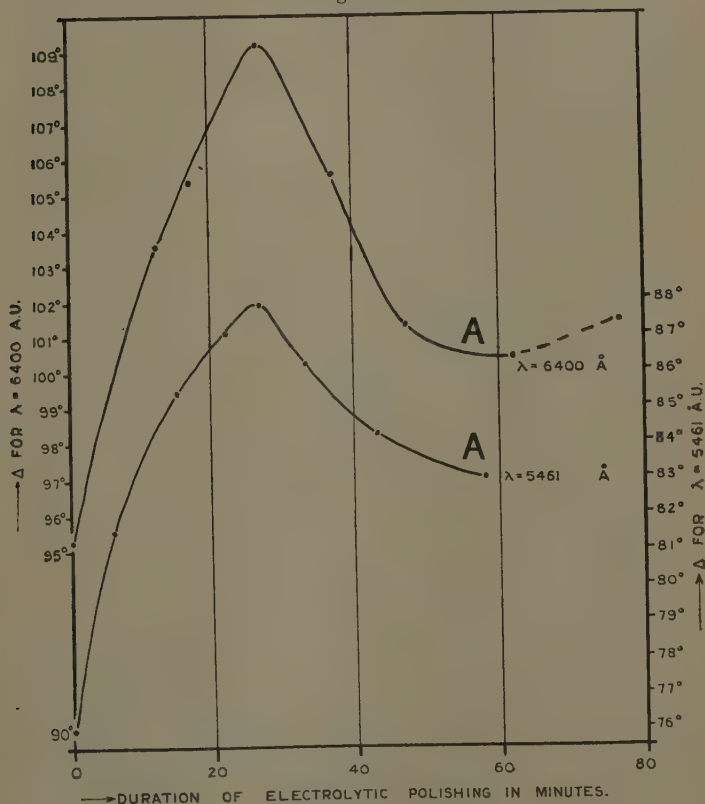
5. *The Change in the Constants as the Mechanical Polish is removed Electrolytically.*

Two experiments were carried out using specimen A for the wave-length 6400 \AA. and specimen B for wave-length 5461 \AA. (mercury arc). The values Δ and 2ψ for specimen A polished mechanically and for 12 minutes electrically (first point of decay curve) were already known. These values of Δ were corrected by extrapolation from the decay curves to the time at which polishing ceased, and gave the first two points of the curve fig. 4.

Specimen A was polished electrolytically for further periods of 5, 10, 10, etc. minutes (see Table II.), and

Δ and 2ψ measured after each additional period. The conditions of polishing, solution, separation of electrodes, voltage, etc. were kept constant throughout. The times of cessation of polishing and the mean times of measurement were carefully noted and corrections for

Fig. 4.



exposure applied to all values of Δ . Readings were taken by two observers alternately.

Specimen B was used to repeat the experiment for the wave-length 5461 Å . in an attempt to follow the variation of the constants to some steady value. Irregularities due to particles of dirt and tiny air-bubbles on the surface,

TABLE II.

Variation of Δ and 2ψ with Duration of Electrolytic Polishing.Specimen A (as at conclusion of time experiment, Table I.). $\theta=70^\circ$ throughout. $\lambda=6400 \text{ \AA}$.

Polishing time in minutes.	Δ (corrected for time decay).	2ψ .
0 (hand polished) * ..	$95^\circ 17'$	$84^\circ 8'$
12.....	$103^\circ 36'$	$88^\circ 1'$
17.....	$105^\circ 24'$	$88^\circ 40'$
27.....	$109^\circ 12'$	$88^\circ 24'$
37.....	$105^\circ 36'$	$87^\circ 41'$
47.....	$101^\circ 18'$	$88^\circ 20'$
62.....	$100^\circ 24'$	$88^\circ 10'$
77.....	$101^\circ 24'$	$87^\circ 48'$

* Taken from results for specimen M.P.A. $\lambda=6400 \text{ \AA}$.

TABLE III.

Variation of n , K , and R with Duration of Electrolytic Polishing.Specimen B. $\theta=70^\circ$ throughout. $\lambda=5461 \text{ \AA}$.

Polishing time in minutes.	Δ (corrected for time decay).	2ψ .	n .	K .	R per cent.
0, hand polished }	$76^\circ 0'$	$66^\circ 34'$	0.94	1.68	50.7
6.....	$81^\circ 35'$	$76^\circ 53'$	0.56	1.98	64.5
15.....	$85^\circ 25'$	$76^\circ 39'$	0.60	2.14	66.3
22.....	$87^\circ 7'$	$77^\circ 9'$	0.59	2.22	68.2
27.....	$87^\circ 57'$	$76^\circ 4'$	0.65	2.24	66.6
33.....	$86^\circ 14'$	$77^\circ 12'$	0.58	2.18	67.8
43.....	$84^\circ 15'$	$76^\circ 14'$	0.61	2.08	64.9
58.....	$83^\circ 1'$	$75^\circ 56'$	0.61	2.03	63.5

slight etching during the adjustment of the current, and slight unevenness of polish resulting in a faintly rippled surface are extremely difficult to avoid in the

Fig. 5.

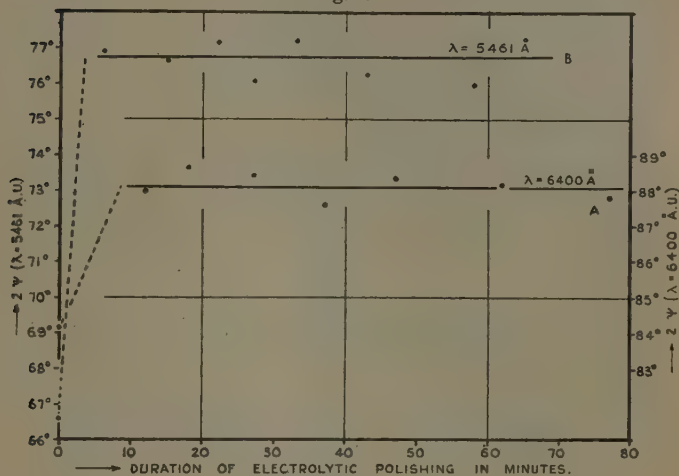
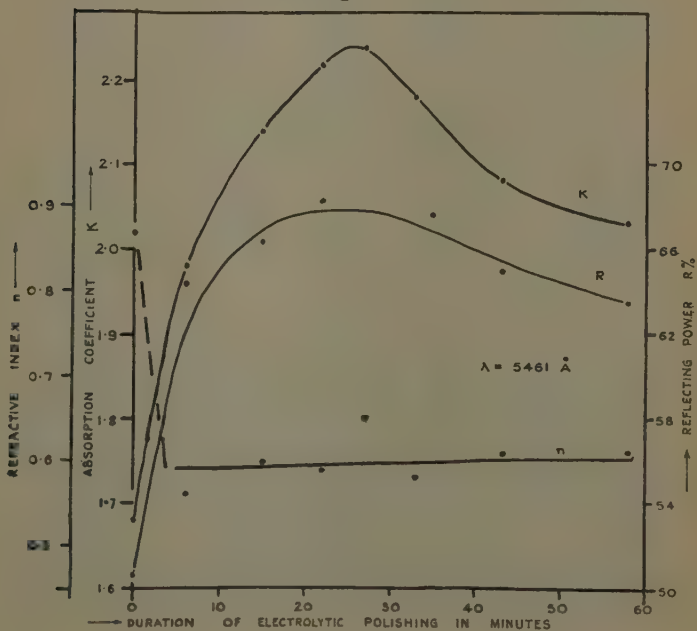


Fig. 6.



polishing process, and, after repeated polishing, marred the surface of the mirror. The resulting field of view had a blotchy appearance which made settings of the compensator and analyzing nicol difficult and inaccurate. Attempts to pursue the curves any further had to be abandoned on this account.

The results are given in Tables II. and III., and the variations of Δ and 2ψ with polishing time are graphed in figs. 4 and 5. The corresponding variations in n , K , and R are shown in fig. 6 for the wave-length 5461 Å.

TABLE IV.

Mechanically Polished Copper.

Specimen A (M.P.A). $\theta = 70^\circ$ throughout.

Wave-length.	Δ .	2ψ .	n	K .	R per cent.
6800 Å. . . .	103° 50'	84° 42'	0.33	3.14	88.7
6700.	100° 3'	84° 31'	0.31	2.92	87.7
6600.	92° 23'	84° 18'	0.31	2.77	86.8
6500.	95° 50'	84° 3'	0.31	2.68	86.0
6400.	94° 8'	84° 8'	0.30	2.60	85.7
6300.	91° 50'	83° 27'	0.32	2.48	83.5
6200.	90° 20'	83° 41'	0.31	2.41	83.6
6000.	86° 2'	82° 8'	0.35	2.11	77.7
5800.	81° 55'	78° 57'	0.48	2.04	70.0
5600.	78° 53'	73° 20'	0.69	1.84	55.7
5400.	80° 25'	68° 7'	0.92	1.86	48.5
5100.	79° 52'	67° 0'	0.96	1.83	46.5
4800.	78° 25'	65° 52'	0.99	1.76	44.0
4358.	75° 1'	63° 3'	1.05	1.63	38.5

The Dispersion Curves of Copper.

Specimens A and B have each been polished mechanically and used to determine the dispersion curves for n , K , and R for copper (curves M.P.A and M.P.B). The same specimens, polished electrolytically, gave two additional sets of dispersion curves (E.P.A and E.P.B). The constants of two independently prepared evaporated mirrors were also measured (curves Ev. 1 and Ev. 2). The values n , K , and R for these six specimens are given in Tables IV. to IX., and plotted against wave-length in figs. 7, 8, and 9.

TABLE V.

Mechanically Polished Copper.

Specimen B (M.P.B). $\theta=70^\circ$ throughout.

Wave-length.	Δ .	2ψ .	n .	K.	R per cent.
6800 Å....	106° 1'	86° 2'	0.25	3.29	91.8
6600.....	104° 53'	86° 1'	0.25	3.21	91.6
6400.....	102° 9'	85° 49'	0.25	3.05	91.2
6300.....	99° 50'	84° 52'	0.29	2.91	88.4
6100.....	95° 43'	84° 52'	0.27	2.68	87.7
6000.....	93° 37'	83° 41'	0.32	2.57	84.5
5800.....	87° 47'	81° 10'	0.41	2.27	77.0
5600.....	83° 32'	75° 3'	0.66	2.05	62.1
5400.....	83° 36'	70° 19'	0.86	2.00	54.0
5200.....	84° 40'	69° 1'	0.92	2.03	52.8
4800.....	82° 25'	67° 59'	0.94	1.93	49.7

TABLE VI.

Electrolytically Polished Copper.

Specimen A (E.P.A). $\theta=70^\circ$ throughout.

Wave-length.	Δ .	2ψ .	n .	K.	R per cent.
6800 Å....	112° 24'	88° 31'	0.11	3.74	97.1
6700.....	111° 42'	88° 25'	0.12	3.68	96.8
6500.....	109° 48'	88° 28'	0.11	3.55	96.9
6400.....	109° 0'	88° 35'	0.10	3.49	97.1
6300.....	107° 30'	88° 37'	0.09	3.39	96.8
6200.....	104° 42'	88° 19'	0.07	3.21	97.5
6000.....	100° 2'	87° 51'	0.13	2.93	94.9
5800.....	93° 55'	84° 31'	0.31	2.59	85.4
5600.....	90° 31'	77° 54'	0.58	2.38	71.3
5400.....	92° 13'	72° 55'	0.84	2.40	63.3
5100.....	92° 16'	71° 39'	0.90	2.39	61.3
4800.....	90° 21'	70° 15'	0.94	2.28	58.1
4358.....	84° 40'	68° 29'	0.95	2.03	52.0

TABLE VII.

Electrolytically Polished Copper.
Specimen B (E.P.B). $\theta=70^\circ$ throughout.

Wave-length.	Δ .	2ψ .	n .	K.	R per cent.
6800 Å. . . .	107° 28'	88° 25'	0.11	3.47	96.7
6600.	105° 23'	88° 31'	0.09	3.25	96.8
6400.	101° 24'	88° 42'	0.08	3.01	97.0
6200.	98° 38'	88° 25'	0.09	2.85	96.2
6000.	94° 10'	87° 21'	0.14	2.61	93.3
5800.	87° 55'	84° 8'	0.27	2.30	84.0
5600.	84° 17'	78° 49'	0.50	2.10	70.2
5400.	85° 32'	74° 44'	0.69	2.13	62.7
5100.	85° 41'	73° 11'	0.76	2.12	60.1
4800.	83° 26'	72° 39'	0.76	2.02	57.7
4358.	78° 11'	70° 53'	0.79	1.80	51.0

TABLE VIII.

Evaporated Mirror.
Specimen I. (Ev. 1). $\theta=70^\circ$ throughout.

Wave-length.	Δ .	2ψ .	n .	K.	R per cent.
6700 Å. . . .	105° 22'	86° 29'	0.22	3.24	92.5
6600.	105° 48'	86° 39'	0.22	3.27	93.0
6500.	104° 0'	86° 9'	0.24	3.16	91.8
6300.	101° 54'	85° 27'	0.27	3.03	90.0
6000.	95° 32'	83° 42'	0.33	2.67	85.0
5800.	91° 3'	80° 18'	0.47	2.42	76.4
5600.	88° 43'	75° 7'	0.70	2.27	65.2
5400.	89° 0'	70° 50'	0.90	2.23	58.2
5200.	89° 19'	69° 52'	0.94	2.23	56.9
5000.	88° 54'	69° 41'	0.95	2.21	56.4
4600.	83° 32'	67° 31'	0.98	1.97	49.7

TABLE IX.

Evaporated Mirror.

Specimen II. (Ev. 2). $\theta=70^\circ$ throughout.

Wave-length.	Δ .	2ψ .	n .	K.	R per cent.
6700 Å. . . .	102° 12'	86° 0'	0.24	3.05	91.2
6500	100° 24'	85° 36'	0.25	2.94	90.1
6300	97° 10'	84° 52'	0.28	2.76	88.0
6200	95° 13'	83° 55'	0.32	2.65	85.5
6100	93° 14'	83° 11'	0.35	2.55	83.3
6000	92° 42'	81° 43'	0.42	2.51	80.0
5800	86° 0'	77° 58'	0.55	2.17	69.2
5600	84° 37'	72° 39'	0.77	2.06	58.3
5400	85° 4'	69° 34'	0.91	2.05	53.8
5100	85° 40'	67° 52'	0.98	2.05	51.8
4800	83° 44'	67° 3'	1.00	1.97	49.4
4358	78° 58'	65° 2'	1.03	1.77	43.3

Fig. 7.

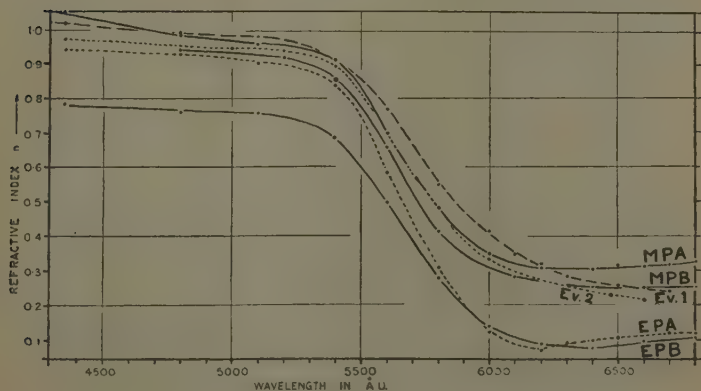


Fig. 8.

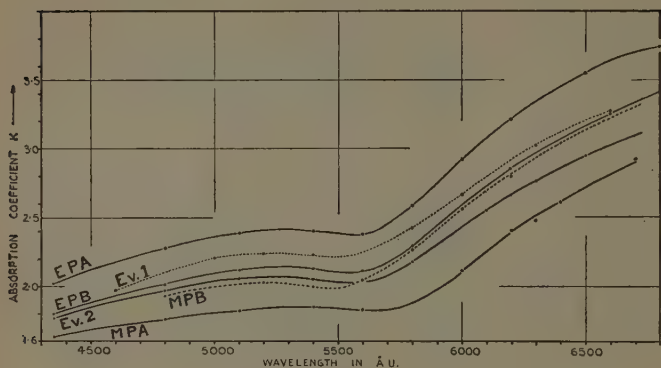
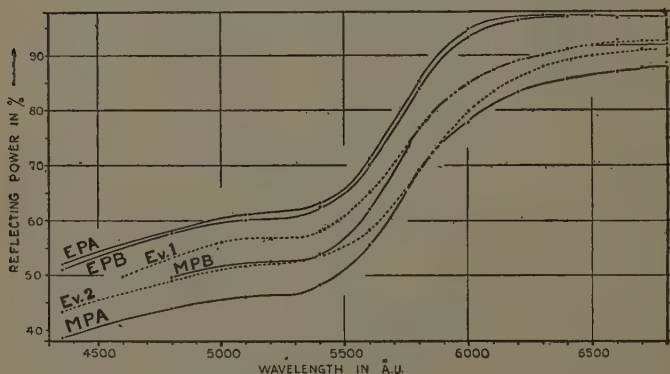


Fig. 9.



III. DISCUSSION OF RESULTS.

Exposure.

It will be seen from Table I. that no change in 2ψ results from exposure; the values are constant and within experimental error up to 30 hours exposure.

There is a rapid decrease in Δ for the first few hours (Table I., fig. 3), after which the curve gradually flattens and becomes almost parallel to the time axis after 14 hours. The total decrease in Δ from the extrapolated values

at zero time to the final level is approximately 4° , and is the same for both the red (6400 Å.) and the green (5461 Å.) wave-lengths. This would justify the application of similar corrections to results for all the wave-lengths used.

The surface after 30 hours appeared to be but slightly tarnished in comparison with the well-known appearance of tarnished copper after several days exposure. The approach of Δ to a constant value after only 12 hours exposure is possibly explained by the hypothesis that the first thin film of oxide formed protects the metal, so that further oxidation is relatively slow.

The Electrolytic Removal of the Mechanically Polished Surface

Interesting variations in the measured constants occur as the surface layers, resulting from mechanical polishing, are removed by the electrolytic process. The phase difference Δ increases rapidly from the value corresponding to a mechanical polish, passes through a maximum, and then decreases (fig. 4). The final points on the curve suggest that Δ would ultimately approach some steady value. No very accurate measurement or estimate of this value has been made, for the reasons stated in section II. of this paper.

The effect upon 2ψ is to produce an apparently discontinuous rise of the order of 5° to 10° after even the shortest practicable period of polishing. A prolongation of the polishing time produces no further changes in 2ψ ; the values remain approximately constant. In making a comparison of the curves for the two wave-lengths it is necessary to point out that the values of Δ and 2ψ for mechanically polished surfaces, which form the starting-points of the curves, are themselves subject to variations associated with the production of a flowed surface. Furthermore, the accuracy with which 2ψ may be determined is lower than the normal accuracy of measurement (viz. $10'$ – $15'$) on account of the deterioration of the mirrors due to prolonged and repeated electrolytic polishing, and this accounts for the rather scattered points in fig. 5.

The changes in the values of the measured constants are, however, of the same order of magnitude for both

wave-lengths, and the maximum values of Δ occur in both cases after a period of approximately 27 minutes polishing.

A high degree of accuracy cannot be claimed for the times of polishing shown, nor is it possible to give very exactly the thicknesses of surface removed. During the first 15-20 seconds of each period of polishing conditions in the cell are unstable, and whilst copper is being removed continuously, the rates of removal during the initial period of adjustment and after the true polishing begins may differ.

The rate of removal of copper from the anode under the same conditions as those under which the specimens were polished has been determined by weighing a small sheet of copper similar to the specimen before and after a lengthy period of polishing.

It was estimated that one minute's polishing corresponds to the removal of a thickness of 478×10^{-7} cm. (4780 Å.). This rate would be sufficient to remove the Beilby layer in less than one minute, a shorter period of polishing than any we have been able to give. Recent estimates of the thickness of the Beilby layer have been made by Hopkins ⁽⁶⁾ and by Lees ⁽⁷⁾, who performed series of experiments on the diffraction of electrons from the polished surface, the surface being removed by sputtering (Hopkins) or by electrolytic etching (Lees). Hopkins, working with gold, obtained a diffraction pattern of two diffuse rings with a mechanically polished surface, and, after removing a thickness of 10 Å., found rings corresponding to various spacings for gold. Beyond 30 Å., which is his estimate of the thickness of the Beilby layer, he found a gradual increase in crystal size, accompanied by increasing resolution of the rings, and at 500 Å. obtained the normal sharp pattern of gold. Lees, from experiments on copper, demonstrated the existence of an oriented layer of crystals beneath the Beilby layer. This orientation was present at a depth of 175 Å. and was believed to be formed by compression. At a depth of 850 Å. the oriented layer had been passed. The crystal size at this depth was 100 Å.

It is suggested that the sudden rise in 2ψ from the value corresponding to a mechanical polish is due to the removal of the Beilby layer (30-40 Å.), the increasing crystal size, and oriented crystals below this layer having

apparently no further effect on 2ψ . The maximum for Δ , however, is not reached until after 27 minutes polishing—that is, until a thickness of $27 \times 0.000478 = 0.00129$ cm. of copper have been removed. It would seem then that the surface has been disturbed during mechanical polishing to a depth far greater than that occupied by the Beilby layer. Such a disturbance might take the form of a breaking up or slight distortion of the metallic crystals, not sufficient to produce a marked effect upon the diffraction of electrons yet affecting the reflexion of light.

It would be logical to argue that Δ attains a constant value only after the complete removal of this disturbed surface. A period of polishing represented by some point beyond A would be required, corresponding to the removal of a surface thickness of 0.0029 cm. or over.

There is, however, a possibility that the decay of the curve for Δ after the maximum is reached is due to the same deterioration in surface after prolonged polishing which we have assumed responsible for the inaccuracy of measurement of 2ψ . In this case the maximum value of Δ after 27 minutes polishing would perhaps be more closely associated with the complete removal of the disturbed metal than the value corresponding to the point A, and the disturbed layer would have a depth of 0.00129 cm.

The Dispersion Curve of Copper.

A comparison of the curves plotted in figs. 7, 8, and 9 for the six specimens shows that different polishing processes produce no essential difference in the form of dispersion curves, but only result in a general raising or lowering of the values of the constants. This parallel shift of dispersion curves with varying polish has been noted by Tool, and the present authors have previously made a comparison between their own results for copper and those of Tool ⁽²⁾ and Minor ⁽⁸⁾. For blue light the authors' values of n and K were of the order of 1.0 and 2.1, and corresponding values of Tool were of the order of 1.2 and 2.3. This increase, it was suggested, was due to the more heavily flowed surface produced by the polishing technique employed by Tool. With the new electrolytic method of polishing used here it becomes definitely clear that the removal of the polished surface is accompanied by a further decrease in n and a rise in K

(compare curves M.P.A and M.P.B with E.P.A and E.P.B).

No correction for the decrease in Δ upon exposure has been made to the dispersion curves. Such corrections would raise the values of n and K for the shorter wave-lengths (measured last) by small amounts. Unfortunately no very exact record has been made of the times taken in the determination of the dispersion curves, as these were undertaken before the investigation into the effects of exposure and electrolytic polishing, when no difficulty was anticipated. For the present curves the order of the correction only is known; n and K would be increased by gradually increasing amounts from the red to the violet, the greatest increase being of the order of 0.01 for n and 0.10 for K .

The wide difference between the curves for mechanically polished specimens M.P.A and M.P.B and the electrolytically polished specimen E.P.B, which was polished for approximately 10 minutes, are explained immediately by referring to the curves showing the changes in Δ and 2ψ with varying polished periods (figs. 4 and 5). The values of Δ and 2ψ for the specimen E.P.B are :—

$$\begin{aligned}\Delta &= 101^{\circ} 24'; 2\psi = 88^{\circ} 42' (\lambda = 6400), \\ \Delta &= 84^{\circ} 50'; 2\psi = 76^{\circ} 30' (\text{interpolated for } \lambda = 5461).\end{aligned}$$

The values of Δ and 2ψ corresponding to a polishing time of 10 minutes for the same two wave-lengths are :—

$$\begin{aligned}\Delta &= 102^{\circ} 30'; 2\psi = 88^{\circ} 20' (\lambda = 6400), \\ \Delta &= 83^{\circ} 50'; 2\psi = 76^{\circ} 40' (\lambda = 5461),\end{aligned}$$

agreeing fairly closely with the observed values.

Although the values of Δ and 2ψ for the specimen E.P.A polished for an unknown period compare well with those obtained after 27 minutes polishing for the same wave-length in the red ($\lambda = 6400$), the values of Δ and 2ψ for such a period do not compare with the actual values observed for this specimen for the wave-length 5461 Å. The observed value of 2ψ is rather lower and the value of Δ considerably higher than those obtained from fig. 4. These yield values of n which are close to those resulting from a mechanical polish. At present we are unable to offer any explanation of this discrepancy.

The general parallelism of the curves is maintained in the absorption coefficient and reflecting powers. The electrolytic surface (specimen E.P.A) gives the highest values of absorption coefficient and reflecting power and the mechanically polished surface (specimen M.P.A) the lowest values. The remaining electrolytic and mechanically prepared surfaces and the evaporated surfaces give intermediate results.

The constants for the evaporated mirrors agree more closely with those for mechanically prepared surfaces than with those for electrolytically polished surfaces, a result which may possibly be attributed to a similarity between the probably minutely crystalline structure of the evaporated film and the amorphous nature of the Beilby layer.

Summary.

Dispersion curves of copper for the visible spectrum have been obtained by Drude's method, using mirrors prepared (i.) by evaporation, (ii.) by mechanical polishing, and (iii.) by an electrolytic method which produces a polished surface free from the amorphous Beilby layer.

The refractive index and absorption coefficient have been observed to decrease and increase respectively upon the removal of the mechanically polished surface by the electrolytic process.

Progressive changes in the optical constants have been studied as increasing depths of the mechanically disturbed surface were removed. The removal of the amorphous Beilby layer, which others have estimated as being 30–40 Å. in thickness, brings about a distinct change in the optical constants, but the mechanical disturbance of the surface extends beyond the Beilby layer to a depth of 0.0013 to 0.0029 cm. or more, and affects the optical constants.

A previous investigation on the effect on the constants of the exposure of copper to the atmosphere has been repeated with more conclusive results.

Acknowledgments.

We wish to express our thanks to Dr. Sykes, of Messrs. Metropolitan-Vickers Electrical Company, to whom we are indebted for the preparation of the

evaporated mirrors, and to Monsieur P. Jacquet, of the Laboratoire d'Électrochimie (Institut de Chimie), Paris, who so generously provided us with information concerning his work on electrolytic polishing, and to whose instructive suggestions and technical details our successful application of his method is entirely due.

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LXIII. *The Thermodynamic Primary and Secondary Dissociation Constants of Maleic and Fumaric Acids.* By WILLIAM L. GERMAN, *M.Sc., Ph.D. (Lond.), A.I.C.*, ARTHUR I. VOGEL, *D.Sc. (Lond.), D.I.C., F.I.C.*, and (in part) GEORGE H. JEFFERY, *B.Sc., Ph.D. (Lond.), A.I.C.*

THE objects of this investigation were: (1) to provide trustworthy values for the true primary and secondary dissociation constants of the two simple cis-trans isomerides, maleic and fumaric acids, and (2) to calculate the inter-carboxylic distances from these values. All previous conductivity and potentiometric work (for literature, see 'International Critical Tables,' vi. p. 265, 1929; Ashton, Thesis, London, 1934) must, in the light of modern standards, be regarded as approximate. New conductivity measurements over the range 0.0001–0.01 N for maleic acid and its sodium salt at 25° have been made, the results for the latter being corrected for hydrolysis and for the presence of carbon dioxide in the equilibrium water employed. The true primary dissociation constant, as evaluated by MacInnes's method (*J. Amer. Chem. Soc.* xlviii. p. 2069, 1926) is 1.20×10^{-2} . Owing to the small solubility of fumaric acid the usual conductivity technique (compare this Journal, xv. p. 401, 1933;

xviii. p. 904, 1934) could not be applied to this acid. Potentiometric titration of both acids was carried out with the quinhydrone electrode at 25° and the true ionization constants evaluated in both cases. From these values the inter-carboxylic distances, r (expressed in Å.U.), were computed by the methods of Bjerrum (B.) (*Zeits. phys. Chem.* cvi. p. 219, 1923) and of Gane and Ingold (G. & I.) (*J. Chem. Soc.* 1931, pp. 2160, 2179). The results are summarized in the following table :—

	$K_{1\text{therm.}}$	$K_{2\text{therm.}}$	r (B.)	r (G. & I.).
Maleic acid	1.20×10^{-2}	5.95×10^{-7}	0.84	2.93
Fumaric acid	9.57×10^{-4}	4.13×10^{-5}	4.05	5.25

Mention must be made of the electrometric titrations of these acids with the quinhydrone electrode by Ashton and Partington (*Trans. Faraday Soc.* xxx. p. 612, 1934; Ashton, *loc. cit.*). These authors have evaluated only the "incomplete" (or classical) dissociation constants, and their results, in so far as they are comparable, owing to the different concentrations at which the titrations were performed, differ considerably from our own.

EXPERIMENTAL.

Preparation of Materials and Solutions.—Pyrex vessels were used throughout, and all solvents were of "AnalaR" purity.

Maleic Acid.—80 grams of Hopkin and Williams' "pure" maleic acid, m.p. 141–143°, were refluxed for 6 hours with 120 grams of redistilled acetic anhydride, the excess of acetic anhydride and acetic acid distilled off and the residue fractionated under atmospheric pressure. The pure anhydride passed over at 196–197° and solidified on cooling; it was recrystallized from chloroform and had m.p. 54°. The pure anhydride was hydrated by evaporating with excess of conductivity water on the water bath and then recrystallized from acetone-light petroleum, b.p. 60–80°. The resultant acid, which was analytically pure, had m.p. 143–144°. This m.p. was unaffected by repeated recrystallization.

The m.p. of maleic acid recorded in the literature is 130–131° (Pelouze, *Annalen*, xi. p. 266, 1834, gives 130°; Kempf, *J. pr. Chem.* lxxviii. p. 239, 1908, states that the acid prepared directly by the hydration of the anhydride,

b.p. $82^{\circ}/14$ mm., had m.p. 130 – 130.5° ; Ashton and Partington, *loc. cit.*, state that Kahlbaum's acid "für Analyse" when "recrystallised several times" (the solvent is not given) has m.p. 131°). The only higher m.p. that appears to be recorded is that by Boeseken and Verkade (*Rec. trav. chim.* xxxvi. p. 170, 1916), who give m.p. 135° for a product obtained by the hydration of the anhydride. The commercially pure samples available to us all had higher melting-points:—Hopkin and Williams' acid, 141 – 143° ; British Drug Houses' acid, 140.5 – 142.5° ; Eastman Kodak Co.'s product, 138 – 139° (see Eastman Organic Chemical List, no. 26, p. 63, 1935). It is difficult to account for the discrepancy. We have found that if the m.p. determination be carried out very slowly (30–40 minutes heating) the acid fuses at 132 – 133° , but this is doubtless due to the depression of m.p. by a little maleic anhydride formed.

Fumaric Acid.—Commercially pure samples had melting-points varying from 275° – 282° (sealed tube). Two samples were prepared from two independent sources; the first was a B.D.H. product and the second Schuchardt's "Acid fumaric pr. anal." The acid was first recrystallized from dilute hydrochloric acid and the product dried in a vacuum desiccator over calcium chloride and potassium hydroxide for several days. It was then crystallized from redistilled dioxan; the separated acid was repeatedly washed with acetone (to remove traces of maleic acid if still present) and then dried in a vacuum desiccator over calcium chloride. The acid then melted at 286° (sealed tube) (Michael, *Ber.* xxviii. p. 1631, 1895, gives m.p. 286 – 287° ; Milas, *J. Amer. Chem. Soc.* xlix. p. 2007, 1927, and 'Organic Syntheses,' xi. p. 47, 1931, m.p. 282 – 284° ; Ashton and Partington, *loc. cit.*, state that their recrystallized product sublimed at 200°).

Sodium Maleate.—This was prepared by dissolving a weighed quantity of the recrystallized acid in absolute ethyl alcohol and adding from a carefully calibrated burette the calculated volume of a standard (approximately N/2) solution of sodium ethoxide, prepared by dissolving Kahlbaum's sodium ("pure for analysis") in absolute alcohol and titrated against standardized hydrochloric acid. The sodium salt gradually separated and, after filtration, was recrystallized by dissolving in a small

quantity of cold water and precipitating it by the addition of absolute ethyl alcohol (Found: Na, as sulphate, 28.72. Calc. 28.76 per cent.).

Conductivity Water.—This was equilibrium water obtained from the still described by Vogel and Jeffery (J. Chem. Soc. p. 1201, 1931).

Sodium Hydroxide Solutions.—These were prepared by the electrolysis of "AnalaR" sodium chloride with a mercury cathode as described by Jeffery and Vogel (this Journal, xv. p. 400, 1933); the amalgam was decomposed in a Jena glass flask with equilibrium water, and the resultant solution, after dilution, standardized, with methyl red as indicator, immediately before use against constant boiling-point hydrochloric acid, prepared by means of the all-glass (Pyrex) apparatus described in J. Chem. Soc. p. 409, 1932. It was necessary to boil the solution vigorously just before the end-point was reached in order to obtain an accuracy of ± 0.01 c.c. in the titration (compare Pregl-Fyleman, 'Quantitative Organic Micro-analysis,' p. 116, 1930). Carefully calibrated burettes were used throughout.

General Technique and Apparatus for Conductivity Measurements.—This has been fully described in J. Chem. Soc. p. 1715, 1931; pp. 400, 2829, 1932, and in this Journal, xv. p. 401, 1933; xviii. p. 904, 1934. Four cells of the Hartley and Barrett type, two of silica, R (0.02586₃) and Q (0.02674₈), and two of Pyrex, S (0.03422₈) and V (0.02781₅); the figures in parenthesis are the cell constants. All measurements were carried out in an electrically controlled water thermostat at $25 \pm 0.01^\circ \text{C}$.

The combined hydrolysis and solvent correction for disodium maleate was computed as described in J. Chem. Soc. 1936, p. 24 (equation 12). The application of a "normal" solvent correction yielded

$$\mu_0^n = \mu_c + 695.6 \text{ C}^{0.606} = 221.4,$$

whence $l_{0_{X''}} = 60.9$ and $l_{0_{HX'}} = 32.3$, since $l_{0_{Na^+}} = 49.6$ and $l_{0_{HX'}} = 0.53 l_{0_{X''}}$. The preliminary value of K_2 , as deduced from the potentiometric titration curve, was taken as 5×10^{-7} .

The experimental results for the sodium salt are given in Table I. κ is the specific conductivity of the water used, $[H^+]$ is the hydrogen ion concentration, $\mu_{\text{obs.}}$ is the molecular conductivity after the application of a normal solvent correction, $\mu_{\text{corr.}}$ that corrected by means of equation (12), μ_0^n is the value of the limiting equivalent conductivity calculated by the "n" formula (Ferguson

TABLE I.

Sodium Maleate. ($M=160.01$.)

$$\mu_0^n = \mu_c + 247.9 C^{0.343}; \mu_0^n = 234.93; l_{0X^n} = 67.7; l_{0HX^n} = 35.9.$$

$C \times 10^4$	$\mu_{\text{obs.}}$	$[H^+] \times 10^7$	$\mu_{\text{corr.}}$	μ_0^n
Run. 1.		Cell V.	$\kappa = 0.768$.	
1.318	218.36	0.690	227.69	—
7.385	212.59	0.123	214.12	234.98
11.94	209.33	0.079	210.21	234.80
25.37	203.06	0.041	203.39	234.88
45.49	197.10	0.025	197.21	(236.15)
60.11	193.76	0.020	193.86	(236.74)
82.25	190.41	0.016	190.48	(238.22)
102.8	187.64	0.014	187.68	—
Run 2.		Cell S.	$\kappa = 0.760$.	
2.688	216.71	0.236	221.31	—
9.251	211.23	0.106	212.36	234.89
17.47	206.56	0.056	206.94	234.96
31.26	200.84	0.033	201.09	235.04
41.21	197.78	0.027	197.90	(235.57)
73.62	191.16	0.018	191.24	—
93.41	188.63	0.015	188.69	—

and Vogel, this Journal, l. p. 971, 1925), the constants of which, together with the limiting conductivity of the anion, l_{0X^n} , are given at the head of the table; M is the molecular weight.

The true primary dissociation constant was calculated by MacInnes's method (J. Amer. Chem. Soc. *xlvi*, p. 2069, 1926) as modified for dibasic acids by Jeffery and Vogel (J. Chem. Soc. 1935, p. 26). A_e was deduced from the relation $A_e H_2A = A_{c'''} HCl - A_{c'''} NaCl + A_{c'''} NaHA$, where c''' is the ionic concentration, for the calculation of which three approximations were necessary. For the acid salt $A_{0NaHA} = A_{c'''} NaHA + xc'''^{0.5}$; x was calculated from the

usual Debye-Hückel-Onsager equation and had a value of 79.3, $\Lambda_{0_{\text{NaHA}}} = 85.7$.

All the relevant results are collected in Table II.: C is the concentration in g. mols./litre, $\mu_{\text{obs.}}$ is the molecular conductivity to which no solvent correction has been applied, K_{class} is the Ostwald ionization constant, K' is the dissociation constant computed from the degree of

TABLE II.

Maleic Acid. ($M=116.03$; $\Lambda_0=383.9$)

$C \times 10^4$.	$\mu_{\text{obs.}}$	$K_{\text{class.}} \times 10_2$.	Δe .	$c''' \times 10^4$.	K' .	$K_{\text{therm.}} \times 10^2$.
Run 1.		Cell C.		$\kappa=0.798$.		
1.136	382.99	(4.711)	—	—	—	—
6.971	362.76	(1.130)	—	—	—	—
10.54	353.24	(0.845)	381.25	9.7666	1.231	1.14
18.86	335.43	1.143	379.78	16.6587	1.259	1.15
31.96	314.37	1.183	378.14	25.5663	1.310	1.16
48.15	295.36	1.236	376.56	37.7697	1.374	1.19
61.70	281.98	1.254	375.50	46.3337	1.397	1.19
75.43	270.75	1.273	374.60	54.5219	1.422	1.20
Run 2.		Cell Q.		$\kappa=0.801$.		
4.411	371.51	(1.279)	—	—	—	—
9.323	356.02	(1.104)	—	—	—	—
14.22	344.78	1.126	380.62	12.8810	1.239	1.14
25.65	323.24	1.151	378.81	21.8873	1.272	1.14
44.30	299.51	1.227	376.90	35.2037	1.363	1.19
67.32	277.25	1.264	375.11	49.7573	1.410	1.20
80.61	267.07	1.283	373.92	57.5932	1.440	1.20
90.45	260.63	1.298	373.19	63.1711	1.463	1.21

dissociation $\alpha = \Lambda/\Lambda_e$, $K_{\text{therm.}}$ is the true dissociation constant deduced from the equation

$$\log K_{\text{therm.}} = \log K' - 1.010 c'''^{0.5}.$$

The values of the true dissociation constant have not been calculated at low concentrations where the influence of secondary dissociation is appreciable.

The values of μ_e for maleic acid and sodium maleate at round concentrations, interpolated with the aid of a flexible spline, are collected in Table III.

General Technique and Apparatus for Potentiometric Measurements.—Full details of this have already been described by us in J. Chem. Soc. 1935, pp. 912, 1628. The measurements were carried out in an oil thermostat maintained electrically at $25 \pm 0.01^\circ \text{C}$. The quinhydrone electrode was used throughout; the hydrogen electrode could not be used owing to the danger of catalytic reduction and the consequent drifting potentials. The cell employed was $\text{Hg}/\text{Hg}_2\text{Cl}_2, \text{KCl (satd.)} \parallel \text{Solution, quinhydrone/Pt.}$; the liquid junction potential was assumed to be negligible. Owing to the slight drift in the E.M.F. values immediately after the addition of alkali, readings were taken only

TABLE III.

$\text{C} \times 10^4$.	Maleic acid.	Sodium maleate.
1.0	383.3	—
5.0	369.7	216.95
10.0	355.5	211.75
20.0	333.3	205.60
30.0	316.5	201.45
40.0	302.7	198.15
50.0	291.7	195.63
60.0	282.9	193.55
70.0	275.8	191.55
80.0	269.9	190.35
90.0	264.8	189.08
100.0	260.0	187.95

when a steady value was attained (usually after about 30 minutes). Before and after each titration the saturated calomel electrode was standardized against at least two independent N/10 calomel cells (compare Clark and Lubs, J. Biol. Chem. xxv. p. 483, 1916), for which a value of 0.3376 volt was assumed (Clark, 'The Determination of Hydrogen Ions,' 1928, p. 480); the resultant value of the saturated calomel electrode, $E_{\text{sat. cal.}}$, sometimes varied within a fraction of a millivolt in different titrations, and it was therefore necessary to use the value obtained in the associated standardizations. The cell system was further standardized against Walpole's acetate buffers (J. Chem. Soc. cv. p. 2514, 1914; compare Britton, 'Hydrogen Ions,' 1932, p. 217) and against M/20 potassium hydrogen

phthalate (Clark, *loc. cit.* p. 486 ; MacInnes and Belcher, J. Amer. Chem. Soc. liii. p. 3325, 1931).

The p_H values were computed from the formula for the quinhydrone electrode : $E = E_0 + (RT/F) \log a_H$. The normal potential of quinhydrone at 25° was taken as 0.6997 volt (Harned and Wright, J. Amer. Chem. Soc. lv. p. 4586, 1933 ; compare Billmann and Krarup, J. Chem. Soc. cxxv. p. 1954, 1924). Hence

$$E = E_{\text{obs.}} + E_{\text{sat. cal.}} = 0.6997 + 0.0591 \log a_H \text{ at } 25^\circ,$$

$$\text{or } -\log a_H = p_H = (0.6997 - E_{\text{sat. cal.}} - E_{\text{obs.}})/0.0591.$$

TABLE IV.

Potentiometric Titration of 100 c.c. of 0.01 N Acid against *ca.* 0.01 N Sodium Hydroxide Solution.

c.c. of NaOH.	Maleic acid. p_H .	Fumaric acid. p_H .	c.c. of NaOH.	Maleic acid. p_H .	Fumaric acid. p_H .
0.00	2.429	2.732	50.00	4.414	3.734
10.00	2.546	2.912	60.00	5.562	4.001
15.00	2.631	2.996	65.00	5.788	4.137
17.50	2.672	—	67.50	5.893	—
20.00	2.716	3.090	70.00	5.985	4.276
22.50	2.766	3.139	72.50	6.073	4.345
25.00	2.814	3.188	75.00	6.144	4.414
27.50	2.864	3.238	77.50	6.242	4.494
30.00	2.942	3.287	80.00	6.330	4.766
32.50	3.008	3.339	82.50	6.425	4.661
35.00	3.088	3.389	85.00	6.519	4.766
40.00	3.287	3.497	90.00	6.729	5.010

Results.—Table IV. gives the mean values of p_H of the titration of N/100 acid against approximately N/100 sodium hydroxide solution for the two acids. The alkali was 0.01030 N for fumaric acid and 0.01016 N for maleic acid.

Fumaric Acid.—The values of $K_{1\text{class.}}$ and $K_{2\text{class.}}$ were computed by Britton's method (J. Chem. Soc. cxxvii. p. 1906, 1925) and are incorporated in Table V. for com-

parison with published data. The thermodynamic dissociation constants were computed from

$$pK_{1\text{therm.}} = pK_{1\text{class.}} + 0.505\mu^{0.5};$$

$$pK_{2\text{therm.}} = pK_{2\text{class.}} + 1.515\mu^{0.5},$$

where $pK_{1\text{therm.}} = -\log K_{1\text{therm.}}$, etc., and μ is the total ionic strength. These expressions were sufficiently accu-

TABLE V.
Fumaric Acid.

Pairs of points used.	$K_{1\text{class.}} \times 10^3.$	$K_{2\text{class.}} \times 10^5.$	$\mu \times 10^3.$	$K_{1\text{therm.}} \times 10^4.$	$K_{2\text{therm.}} \times 10^5.$
10.00 } 60.00 }	0.985	5.39	2.26 4.97	(9.34)	(4.22)
15.00 } 65.00 }	1.019	5.28	2.45 5.28	9.63	4.10
20.00 } 70.00 }	1.023	5.26	2.62 5.46	9.65	4.07
22.50 } 72.50 }	1.019	5.29	2.71 5.65	9.59	4.07
25.00 } 75.00 }	1.017	5.39	2.82 5.83	9.57	4.13
27.50 } 77.50 }	1.013	5.38	2.92 6.04	9.52	4.10
30.00 } 80.00 }	1.022	5.44	3.04 5.98	9.59	4.16
32.50 } 82.50 }	1.019	5.54	3.16 6.38	9.55	4.19
35.00 } 85.00 }	1.036	5.54	3.28 6.60	9.50	4.18
		Mean	9.57	4.13

ate for the dilute solutions employed. μ was calculated from the equation

$$\mu = 0.5 \left(a + h + c \left\{ \frac{1}{(h/K_1 + 1 + K_2/h)} + \frac{4}{(h/K_2 + 1 + h^2/K_1 K_2)} \right\} \right),$$

where c = total acid concentration, h = hydrogen concentration, and a = concentration of sodium hydroxide added (German, Jeffery, and Vogel, J. Chem. Soc. 1935, p. 1629).

Maleic Acid.—Here $K_1 \simeq 5 \times 10^5 K_2$ so that independent calculations of K_1 and K_2 are possible. For a dibasic acid, H_2A , of this type the alkali, up to the first equivalent, reacts only with the hydrions arising from the first stage of ionization, and thereafter it reacts, to the second equivalent, with those from the second dissociation. The salts $NaHA$ and Na_2A are assumed to be completely dissociated. The Henderson-Hasselbach equation in

TABLE VI.
Maleic Acid.

cc. of NaOH.	$K_{1\text{class.}}$ $\times 10^2$.	$K_{2\text{class.}}$ $\times 10^7$.	$\mu \times 10^3$.	$K_{1\text{therm.}}$ $\times 10^2$.	$K_{2\text{therm.}}$ $\times 10^7$.
10.00	1.27	—	3.77	1.18	—
15.00	1.25	—	3.67	1.17	—
17.50	1.22	—	3.64	1.14	—
20.00	1.27	—	3.62	1.18	—
22.50	1.22	—	3.58	1.14	—
25.00	1.27	—	3.57	1.18	—
27.50	1.33	—	3.56	1.24	—
30.00	1.11	—	3.55	1.03	—
32.50	1.13	—	3.47	1.06	—
35.00	1.11	—	3.45	1.05	—
40.00	1.15	—	3.42	1.08	—
Mean				1.14	
60.00	—	7.73	4.49	—	6.12
65.00	—	7.69	4.97	—	6.02
67.50	—	7.56	5.20	—	5.86
70.00	—	7.58	5.43	—	5.88
72.50	—	7.60	5.64	—	5.84
75.00	—	7.78	5.85	—	5.96
77.50	—	7.73	6.05	—	5.89
80.00	—	7.80	6.25	—	5.92
82.50	—	7.84	6.45	—	5.93
85.00	—	8.04	6.63	—	6.05
				Mean	5.95

dilute solution reduces to (compare Glasstone, 'The Electrochemistry of Solutions,' 1930, pp. 189-190)

$$pK_{1\text{class.}} = p_H + \log ([\text{Acid}] - [H']) - \log ([\text{Acid salt}] + [H'])$$

$$= p_H + \log ([y/2 - x] - [H']) - \log ([x] + [H']),$$

where y = number of c.c. of alkali required for complete neutralization of the acid, x is the actual number of c.c. of alkali added corresponding to the observed p_H .

Similarly,

$$pK_{2_{\text{class.}}} = p_H + \log ([\text{Acid salt}] - [\text{H}']) - \log ([\text{Normal salt}] + [\text{H}']) \\ = p_H + \log ([y - x] - [\text{H}']) - \log ([x - y/2] + [\text{H}']).$$

The thermodynamic dissociation constants were then calculated as described under fumaric acid. The results are collected in Table VI.

The distances between the two carboxyl groups, r , have been calculated by Bjerrum's expression (*Zeits. phys. Chem.* cvi. p. 219, 1923) $P_2 - P_1 - \log 4 = 3.1 \times 10^{-8}/r$, where $P_2 = -\log K_2$ and $P_1 = -\log K_1$, and also by Gane and Ingold's improved expression (see *J. Chem. Soc.* 1931, pp. 2160, 2179), which takes into account the change in properties of the solvent. The results are :—

Acid.	$K_{1\text{therm.}}$	$K_{2\text{therm.}}$	$r(\text{B.})$	$r(\text{G. \& I.})$
Maleic	1.20×10^{-2}	5.95×10^{-7}	1.19	2.90
Fumaric	9.57×10^{-4}	4.13×10^{-5}	4.05	5.25

The values for the inter-carboxylic distances thus calculated may be compared with those computed from the known atomic dimensions : the distance C—C is 1.54 Å., C=C 1.32 Å. (Sidgwick, *The 'Covalent Link in Chemistry,'*

1933, p. 82), the angle $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$ is assumed to be 125°, and

the distance from the nucleus of the carbon atom to the centre of action of the charge on the carboxylate ion is taken as 1.00 Å. (Gane and Ingold, *J. Chem. Soc.* 1931, p. 2164; compare Ingold and Mohrhenh, *ibid.* 1935, p. 949). The results obtained from this model are for maleic acid 4.25 Å. and fumaric acid 5.91 Å. This agreement with the result derived by Gane and Ingold's method must be regarded as satisfactory in view of the fact that no allowance has been made for the propagation of electrical influences through the double bond.

The Authors' thanks are due to the Royal Society and Imperial Chemical Industries for grants. The conductivity work described in this paper was carried out at University College, Southampton.

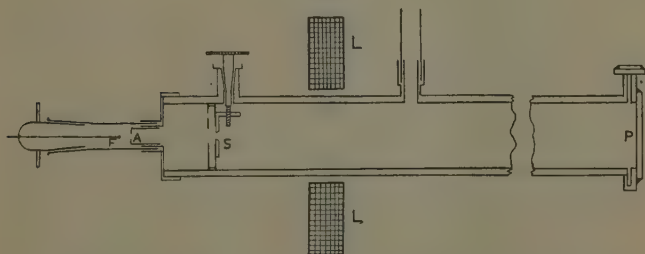
Woolwich Polytechnic,
London, S.E.18.
14th May, 1936.

LXIV. *A new Effect observed on passing Electron Beams through Narrow Slits.* By WALTER MCFARLANE, M.A., B.Sc., Lecturer in Natural Philosophy in the University of Glasgow*.

[Plate V.]

IN the course of some experiments with electron beams some remarkable effects were obtained when the electrons were passed through narrow rectangular slits with a width of the order of a tenth of a millimetre. The emergent beam exhibited a band-like structure with bands falling inside the geometrical shadow of the slit, the patterns being reminiscent of diffraction phenomena, but due, as experiments showed, to a distribution

Fig. 1.



of electric charges on the slit-edges, and probably related in some way to minute irregularities on the edges.

Such an effect should be of considerable importance in electron optics, since it will affect the electron images of small apertures. It is also possible that it might lead to the production of spurious spots or bands in electron diffraction patterns where the beam is limited by a small aperture. This would particularly apply to the use of the slow electrons.

Experimental Arrangements.

The effect was first observed with the arrangement illustrated in fig. 1. Electrons emitted from a straight filament F (0.1 mm. in diameter and about 1.5 cm. long) are accelerated towards the anode A, which contains

* Communicated by the Author.

a slit (2×10 mm.). The beam encounters the slit S, which is adjustable in width by a screw operated through a ground-joint. The length of the slit is determined by masks screwed on to the slit carrier. The electrons which pass through S fall on a zinc-sulphide fluorescent screen P or on a photographic plate which can be inserted in front of P. The tube was of copper, 5 cm. internal diameter, the distances F to S 6.5 cm. and S to P about 100 cm. The accelerating potentials were supplied by dry batteries, and varied from about 300 to 1000 volts, the tube, including the anode and slit, being earthed.

In the main tungsten filaments were found preferable to oxide cathodes, because they showed more regularity in emission along their lengths. Any irregularities were transmitted to the screen patterns.

No electrostatic focusing was used to increase the beam current, since this would necessarily interfere with the rectilinear propagation of electrons from the filament through the slit.

A disadvantage of the above simple arrangement is that light emitted by the filament falls on the screen or plate and in some cases interfered with photography. When necessary a short bent tube was inserted between the filament carrier and the main tube, the electrons being deflected towards S by means of small Helmholtz coils.

A magnetic lens L could be used to obtain on the screen an enlarged image of the filament or slit when desired.

The photographic plates used were Ilford Process, sensitized with a thin film of Apiezon B oil. The latter was tried because of its low vapour-pressure, and proved very effective as a sensitizer.

The sides of the slit S consisted usually of two small plates (about 10×6 mm.) which could be fixed to the sliding pieces shown in the figure. The edges forming the edges of the slit were made as straight as possible and thoroughly cleaned before mounting by frequent immersion in benzol, ether, or acetone.

The experiments were conducted in high vacuum, the pumping system consisting of Metropolitan-Vickers oil-diffusion pumps 02 and 03 in series.

Description of Experiments.

The effect which this paper purports to describe was first observed when the slit S in the arrangement of fig. 1

was made very narrow. With a wide slit (about 1 mm.) the screen image consisted simply of a broad band with ill-defined edges similar to an optical image. On moving the sides gradually together there appeared, when the slit-width was of the order of 0.2 mm., a number of lines parallel to the slit closely crowded together. Further diminution in the width caused the whole screen image to open out and the lines to show up more clearly. The lines occupied positions well inside the optical shadow of the slit sides. Over a certain range of slit-width the lines remained sharp, but with an exceedingly narrow slit (about 0.02 mm.) the lines themselves as well as the whole screen pattern became broader and more diffuse.

The whole effect bears a striking resemblance to optical diffraction at a slit, but the distance between the lines is much too large to admit of such an interpretation. On the other hand, the distance is much too small for the lines to be due to reflexion from the crystal planes of the metallic slit edges.

Fig. 2 (Pl. V.) shows the pattern obtained with a slit formed of copper knife-edges, the width being 0.095 mm. and anode-voltage $V=475$. This pattern occurred at some width with many slits. There appear two intense broad bands with fainter lines between them and outside them, suggesting a symmetrical arrangement. Fig. 3 (Pl. V.) shows the result of reducing the width to 0.053 mm. The lines have spread out but changes have taken place in the relative intensities of the lines and in their arrangement. These changes, combined with the smallness of the slit-width, rendered very difficult any attempt to discover the quantitative relation between slit-width and the separation of the lines. Of the observations which were made, however, many suggested that for a certain range at least the distance between any two lines was inversely proportional to the slit-width.

The pattern obtained with an exceedingly narrow slit is illustrated in fig. 4 (Pl. V.), which was obtained with brass edges 0.025 mm. apart ($V=520$ volts). Fig. 5 (Pl. V.) shows a remarkable photograph obtained with aluminium knife-edges (slit-width=0.09 mm., $V=395$ volts). The whole pattern consists of a large number of very fine lines. At least forty can be counted on the plate.

The width of the pattern and the distances between its constituent lines were found to depend on V , decreasing

as V was increased. By selecting two of the stronger lines in any case it was possible to obtain, from measurements on the screen, the relation between V and the separation of the lines. The distance between the lines was always, within the range of experimental error, inversely proportional to V . This result in itself definitely excludes any diffraction phenomenon which would require a separation proportional to the wave-length, *i. e.*, inversely proportional to \sqrt{V} .

The intensity of the beam passing through the slit could be regulated by adjustment of filament temperature. Alteration in beam current, other conditions remaining unchanged, produced no appreciable change in the screen pattern other than in the intensity of the lines.

An experiment was tried in which the sides of the slit were mounted on a small plate which was supported by a copper wire passing through a glass stopper fitted into the ground-joint. In this way the slit could be charged to any desired potential. When the potential was made negative relative to the tube and gradually increased the lines came closer together until they formed a narrow closely packed bundle. Further increase in potential caused them to cross over and open out again. A positive charge simply increased the separation of the lines. These observations suggest that the lines are produced by electrons attracted towards each edge of the slit by positive charges. The effect of these charges would be gradually neutralized by the addition of negative charges.

A large number of different slits was tried in order to find if any regularity or symmetry could be associated with any particular metal or shape of edge, but no definite results could be obtained. Slits with edges of the same shape and material gave different patterns. In general the lines were obtained more easily and at greater widths of slit when the edges were flat or rounded. With very sharp edges, such as pieces of razor blade, very fine sharp lines were formed with widths of the order of 0.02 mm.

By gradually increasing the current through the magnetic lens it was possible to observe during the focusing process the source of the electrons for any given line. Each line was observed forming from a very small portion

of the slit. The slit seemed to be divided longitudinally into small sections through each of which the electrons formed a separate image of the filament in the manner of a pin-hole image in optics. In this case, however, a displacement perpendicular to the slit is added. The

Fig. 6(a).

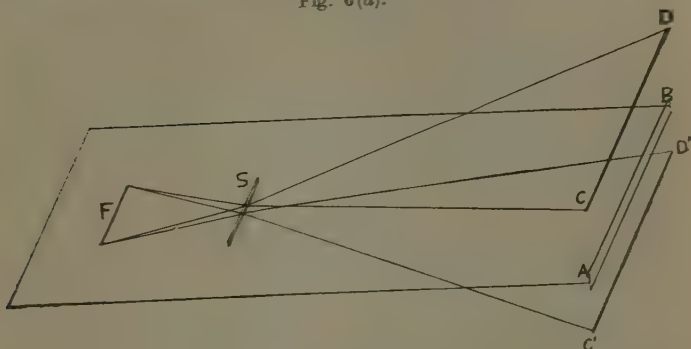
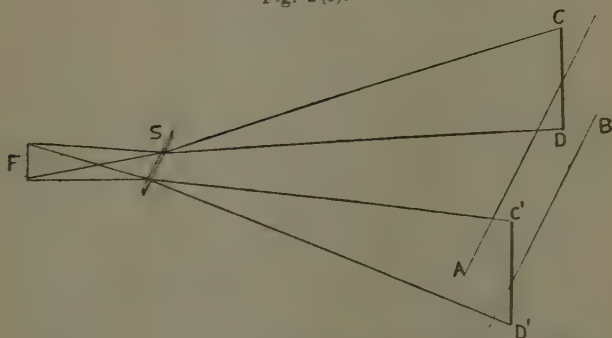


Fig. 6(b).



F=filament : S=slit : AB=geometrical projection of slit ;
CD, C'D'=electron images of the filament.

process is illustrated in fig. 6 (a). The above observation was confirmed by arranging a shutter which could reduce the effective length of the slit. Lines disappeared as the shutter was moved along the slit.

The above experiments suggested that interesting results would be obtained if the filament were rotated

into a position normal to the slit. The result obtained in this manner with two razor-blade edges is shown in fig. 7 (Pl. V.) (slit 2×0.1 mm., $V=920$ volts). In order to limit the size of the pattern the anode aperture was made circular of 1 mm. diameter. Thus the lines of the photograph are to be regarded as images of this length of filament. The irregularities in intensity along the length of the lines are due to variation in emission. In this photograph is shown very clearly how the slit seems to be divided along its length into separate parts each of which produces a separate image of the filament. Here the displacement which rendered the lines visible at all in the previous experiments is represented by a displacement of the whole filament image along its own length. The formation of a line is illustrated in fig. 6 (*b*). This displacement perpendicular to the slit varied in the same way as before with anode potential and width of slit. For any given slit the rotation of the filament produced a rotation of the line about its mid-point.

The fact that the lines on the photographs are magnified inverted images of the filament was easily demonstrated by using a V-shaped filament. The lines were replaced by V's which were inverted with respect to the filament in every position in which the filament was placed. A strange feature of the patterns, however, is that the lines are definitely narrower than an optical image of the filament would be. The filament was 0.1 mm. in diameter, and the magnification being about 15 the optical image would be about 1.5 mm. in width.

The lines are much more readily obtained with the filament normal to the slit, and appear with quite wide slits. Thus fig. 8 (Pl. V.) shows a photograph taken with a slit-width of 0.44 mm. ($V=870$ volts). A magnified electron image of the slit produced by the lens accompanies the screen pattern. This slit was made of aluminium, the edges being rounded into cylindrical shape and highly polished with fine rouge powder. The photograph shows clearly that the lines are produced at the two slit edges, the lines on each side being quite independent of the other. The effect of making the slit very narrow was to cause the two sets of lines to intermingle and produce a pattern similar to fig. 7 (Pl. V.). All the electrons passing through the slit are forced into the lines.

Fig. 9 (Pl. V.) shows the pattern obtained with a point

source formed by a spot of calcium oxide on a platinum wire (slit with flat zinc sides, 0.1 mm. apart, $V=650$ volts). Here the displacement perpendicular to the slit and the separation into numerous images of different intensity are also clearly shown.

It seemed fairly certain that the formation of the lines could not be traced to gas layers on the edges since the slits were under bombardment by electrons over long periods without showing any change of pattern. In order to remove any doubt a slit was made of folded platinum foil (the folds forming the slit edges) through which a heating current could be passed. No change occurred in the pattern after maintaining the foil at red heat over a period of about twelve hours.

Discussion.

The above experiments suggest that the division of the slit into small parts, each producing a separate filament image, is due to a distribution of charges along the edges of the slit. Since extreme care was taken in the cleaning and mounting the possibility of the presence of grease or other insulating matter is exceedingly remote. It was found, however, that when small projections did exist on the edges, although these were of small dimensions relative to the slit-width, they exerted repulsive forces on all the electrons right across the width of the slit, this no doubt being due to an accumulation of negative charge on or near the projections. Thus it was found possible to associate the less intense regions in fig. 7 (Pl. V.) with such small projections which were visible in a microscope. This suggested immediately that the apparent regularity in the spacing of the lines in this pattern would be due to a corresponding regularity in the microscopic serrations which might be produced on the razor-blade during the process of machining it. No such correspondence could, however, be detected.

As an aid to discovering whether irregularity of the edges contributed to the production of the lines edges with easily visible regular serrations (12 per mm.) were employed. This slit provided patterns similar to those illustrated above, and it was easily shown by gradual focusing that some of the lines were attributable to electrons passing through the depressions on the edges, while in general the electrons suffered repulsion at the

projections. The magnetic lens image of the slit itself showed points of intensity in the depressions. (Such points could also be detected sometimes in the images of slits with only microscopic serrations, and, indeed, are visible in the slit-image shown in fig. 8 (Pl. V.).) These observations suggest the existence of a positive charge in the depressions and a negative charge in the projections. It is extremely doubtful, however, whether the lines in the cases of the straight edges with microscopic serrations are to be associated with the minute depressions which, of course, must always be present, but can easily be made of negligible dimensions compared to the width of the slit. The slit used for fig. 8 (Pl. V.) was made with highly polished round edges so as to minimize the magnitude of the serrations as far as possible, and still it showed a very clear pattern of fine lines, for which no corresponding depressions or projections could be discovered with the aid of a microscope.

The effect produced by a point-charge on a beam of electrons can easily be worked out. An electron projected with high speed v past a charge E traces a hyperbola, the ultimate angle of deviation from the original path being $\frac{2eE}{mv^2z}$, where z denotes the perpendicular distance

from E to the original direction. This may be written E/Vz , where V is the accelerating potential of the electrons. For the case when E is negative consecutive electron paths intersect, the locus of the point of intersection being a parabola. The effect on a beam is illustrated in fig. 10 (*a*). The rays on falling on a screen would produce a sharp edge at A , at which the intensity would be a maximum, the distance AC being inversely proportional to V and to the width of the slit. These results fit the observations, but when the observed value of the displacement perpendicular to the slit is taken into account the variation of intensity near A is not great enough to explain the sharpness of the lines. In any case the experiments above described suggest that the lines are produced by attraction towards each edge and not by repulsion from it.

A positive point-charge cannot produce a concentration of the beam in any direction, but a spatial distribution of positive ions can. Suppose we consider a homogeneous

spherical distribution of positive charge. This, of course, is purely an abstraction, since it is necessarily not in equilibrium, but it will serve to provide at least some idea of the effect of a local accumulation of positive ions near a point on the edge of the slit. The effect produced on a beam is illustrated in fig. 10 (b). An electron projected towards a sphere, radius R , total charge E , is deviated through an angle given to the first approximation by $\frac{E}{VR} \frac{1 - \cos^3 \alpha}{\sin \alpha}$, where $R \sin \alpha$ is

Fig. 10 (a).

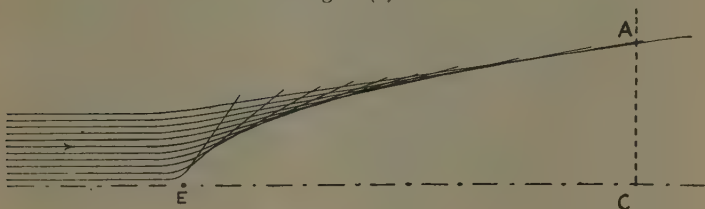
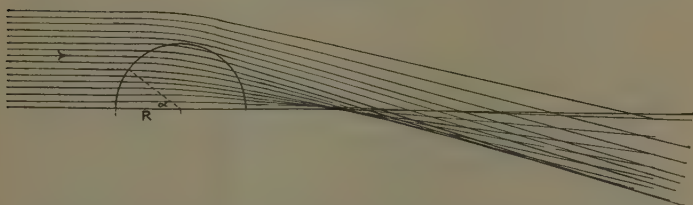


Fig. 10 (b).



the distance from the centre to the original direction. This has a maximum value for $\alpha \doteq 68.5^\circ$, and consequently there will be a concentration in the beam. The concentration, however, is not sufficiently great to appear as a sharp line. Also the variation of displacement with slit-width is not apparent unless an increase in charge accompanies a diminution in width.

It is probable that the formation of the lines depends on the presence of both positive and negative charges as suggested by the experiments with the intentionally serrated edges. If we combine the attractive effect of a positive charge with the focusing effect of two

negative charges, one above and one below, then images similar to those observed would result. Such an arrangement cannot be attacked mathematically, but a consideration of the effect of one negative point-charge as shown in fig. 10 (a) will show that the addition of another above the existing one must produce a concentration of the beam passing between them.

Little has been said regarding the possible source of these charges, which appear on the earthed metallic edges of a slit in a field-free space. Several possibilities must be considered. They may simply be induced by the passage of the beam, they may be local aggregations of space-charge, or they may be related in some way to secondary emission of electrons. It is difficult, however, to reconcile any of these views with the experimental facts that the patterns obtained remain constant over long periods of electron bombardment, and, what is more important, that they do not vary with beam current. Further inquiry is necessary to elucidate this question and to provide a more accurate explanation of the formation of the lines.

The author desires to acknowledge his indebtedness to Prof. Taylor Jones for his helpful advice and criticism.

LXV. *The New Meaning of Gravitation and some Consequences.* By F. TAVANI*.

IF we refer the phenomena of our physical space to a natural frame, such as the frame of which our earth is the origin, we cannot use the original Lorentz transformation, in which the origin moves with a rectilinear and uniform motion, but we must use the transformation of the Cartesian coordinates into those of a frame whose origin describes a curved path †. Let then T be vector unity taken as axis along the tangent to the orbit and N along the normal, $\frac{1}{\rho}$ the curvature of the orbit at a given point.

* Communicated by the Author.

† *Phil. Mag.* p. 187 (July 1934).

We know from the properties of the said axes that $\frac{dT}{dt} = \frac{1}{\rho} N$, and therefore if the origin moves along a straight line $T'=0$ in this case also $\frac{1}{\rho}=0$ and the acceleration $\frac{v^2}{\rho}$ is also $=0$.

Therefore, if the origin instead of describing a curved path describes a straight line, there is no acceleration along N . This is sufficient to prove that there is no force residing in the material body O , taken as the moving origin of the frame; if there were such attracting force there would be an acceleration even when O describes a straight line, which is impossible, because in this

case we have $\frac{1}{\rho}$, and consequently $\frac{v^2}{\rho}=0$. Therefore we

can say that if there is an acceleration $\frac{v^2}{\rho}$ along N ,

$\left(\frac{v^2}{\rho} = \lim_{u_1=v} \left(\frac{u_1 v}{\rho}\right)^*\right)$, the path of O has a curvature $\frac{1}{\rho} > 0$

and $\frac{dT}{dt} \neq 0$, and, reciprocally, if the path of O has a

curvature there is an acceleration $\frac{v^2}{\rho}$ along N . This is

a mathematical proposition established *a priori* to any experience. Experience confirms the proposition and

the acceleration $\frac{v^2}{\rho}$ of a body falling along N we call the

phenomenon of gravitation, a phenomenon without the force which was supposed to be the cause of it, residing within the material bodies.

Having thus eliminated such a force, gravitation is a mere fact or event, a fact of space-time, in which space and time meet, becoming thus such and such event. To the geometrical axes T and N correspond the time as t_1 and t_2 †, given by a watch at rest relatively to origin—that is to say, describing the same path described by the origin. Space-time thus conceived might be merely

* Phil. Mag. p. 839 (November 1935).

† Phil. Mag. p. 1055 (May 1935).

hypothetical, purely a mathematical conception. The test of its reality is to see whether the origin really describes a curved path*, so that while the origin describes a curved path the motion of a body along the normal

N to the curve is accelerated with the acceleration $\frac{v^2}{\rho}$.

Such physical fact for making the space-time physically real is the gravitation. So gravitation may also be considered as a proof of the reality of the space-time above described; this space-time coincides, as far as our experience goes, with our physical space, and it extends as far as gravitation extends. Where is gravitation there is a space-time of the type above studied, and reciprocally where is such space-time there is also the accelerated motion of bodies along N. Such motion is natural in this space, spontaneous and without the intervention of any force to cause it, just as in a space in which the origin moves in a straight path forces are required to cause an acceleration and a deviation from the straight path. On the other hand, as for the presence of some force which at some remote moment would have started the motion of the bodies, ready made, of our planetary system or of beyond them, there is no evidence of the

* NOTE.—As an exercise of pure mathematics we can build many types of space-time, but no reality will correspond to them unless we find in nature that the path described by their point-origins is real. Of such hypothetical nature is the space-time of four dimensions, assumed in the Theory of Relativity. In fact a space-time is characterized by the motion of the origin of the frame and the geometrical dimensions of its path, which must be also the path followed by a clock. In the space-time of Relativity there is assumed that the path described by the origin is a straight line covered with a constant velocity, a path which can hardly be admitted to exist in nature. The space-time of this type is a space-time of two dimensions, one geometrical (or Cartesian) and one temporal. The axes y, z , which are introduced in addition to x and t , are really axes of a Cartesian or geometrical space which have no time correspondent to them. Any motion of the origin along the said axes y and z is not considered. Therefore the four-dimensional space of the Theory of Relativity in reality is nothing more than a two-dimensional space-time, to the points of which are made to correspond univocally points of a geometrical (or Cartesian) space, the space of the axes y and z . For this reason the four-dimension space of Relativity may be well called a pseudo-space-time of four dimensions.

For simplicity we have limited our considerations to the case of the origin describing a plane curve. In reality the path of the earth or any planet is a curve of geometrical (Cartesian) space of three dimensions, and the space-time correspondent to this case is a space-time of six dimensions, as already considered in another note (see Phil. Mag. p. 1056 (May 1935)).

existence of such a moment, characterized by the condition $\frac{dT}{dt} = 0$, in the history of the evolution of the energy, that constitutes our present universe. There is no evidence for supposing any ground on which we can compare the initial moment of motions artificially caused by applying some force or impulse with the motion of our planets or bodies beyond the solar system.

Abandoning thus the intervention of forces described as gravitational, the whole synthesis of our physical world build round the concept of the said forces, accepted by Newton and handed down to us, becomes loosened, and those phenomena which were made intelligible through such concept demand a reinterpretation free from the idea of a Newtonian force.

At the same time any attempt already made of giving to any of those phenomena an interpretation free from the idea of a gravitational force after the elimination of such a concept indirectly gains ground. Of the outstanding phenomena demanding a new interpretation we shall consider weight, the formation of the orbits described by planets and other bodies of our space, and the planetary perturbations from the orbits. The meaning of these phenomena may still remain an object of speculation, and within the object of this note only a hint will be given of a rational view connecting them with the new situation created by the elimination of attracting forces identified till now with the force of gravitation.

Weight cannot any longer be identified with a central force, as intuition would suggest. Let us consider the fact through which weight comes to be an object of our experience: if objects were always falling we would say that all objects have the same weight, we could say also that there is no such a thing as weight, weight would not exist as the characteristic of a body distinguishing it from another, since they all fall with the same velocity. We may think, however, that in their fall they all possess a characteristic, though invisible and not yet an object of experience—that is to say, their own mass or inertia which opposes the acceleration of the fall. This would be a mere inference from what follows the fall, and not from observation. If such characteristic mass, different for each object, exists, the energy necessary to give the same velocity to all objects of different mass must

differ from object to object, though all apparently being in the same dynamical conditions. Such different amount of energy which acts during the fall must remain different also when the fall stops, and the different forms in which it appears when the fall stops constitutes the essence of the weight.

In this meaning of weight, free from the action of a central force acting on the body, mass measures the amount of energy necessary to impart the same velocity to bodies of different mass, and this view of mass as compared with energy agrees with that accepted in modern physics, while the identity of velocity for all bodies of different mass agrees with the new interpretation of gravitation depending for all only on the value of

$\frac{1}{\rho} > 0$ for the spot on which the fall takes place *.

Excluding the bodies moving in consequence of some applied force, we can say, as an immediate consequence of this view of weight, that all bodies either weigh or fall. In the latter case their mass is not an object of experience, but its existence is inferred from the existence of an acceleration ultimately attributed to a mathematical condition realized by motion in our physical space only, T being a function of time †. In the former case mass appears as the measure of the stored energy which was kinetic during the fall of the body.

If the weight of a body represents the stored energy which is necessary to make bodies of different mass cover the same tract of space along N with the same velocity, the mass of the body will be expressed by the formula

$\frac{w}{g^2}$, where w is the stored energy and g the acceleration ‡.

The acceleration can be compared to the velocity of light in the more general formula expressing the mass if we assume for v in the more general formula the value of the accelerated velocity of light §.

* Imagining for the terrestrial gravitation that the origin O describes not the orbit but a parallel of the earth.

† Phil. Mag. p. 838 eq. (4) (November 1935).

‡ Should the old expression $\frac{w}{g}$ of the mass be preferred this would be merely a question of choice, since the two expressions only differ from one another by a constant factor.

§ Phil. Mag. p. 839 (November 1935).

Weight, as object of our experience, under the form of a stored energy, can be compared to a similar manifestation in the motion of an electrified sphere with a surface charge e . The magnetic field superimposed to the electrical field in this case represents localized energy, which would be recovered when the motion is arrested in the form of work done against the retarding actions.

Let us pass to consider the other two problems, which have been so far solved by the intervention of the gravitational force—the origin of the orbits and the planetary perturbations caused by the force of attraction exercised by planets on one another and varying with the law of the inverse square of the distances. There has been already noticed the lack of any evidence, in the history of the evolution of the energy that forms the actual material of our universe, of a moment in which a force may have started the motion directing it in a straight line. In the absence of such a force we are led to two hypotheses about the origin of the orbits: either we attribute them to the structure of our space *, opening to motion nothing but curved paths as shown in the space-time of six dimensions, above described, or we turn to an old hypothesis, that is to say of an electrostatic attraction. Indeed, if there is an attracting force between two bodies of our solar system according to the law $\frac{mm_1}{v^2}$, and if such

force is not gravitational, the next agency we know, acting with the same law and not gravitational, is an electrostatic attraction. At a moment which we may only assume as initial in the study of the motion, with the charge of the body moving along a certain path determined by the conditions of the motion, we may assume irradiation of energy, necessarily followed by a decrease of mass. This state of things, which is not dissimilar from the motion of the charge of an electron at a moment when irradiation was of a certain intensity, must have determined a curvature in the path, a curvature which, while hinting a fall towards a nucleus, remained more or less stationary with the decrease of the irradiation of energy of the moving body.

A residual electrostatic attraction, as was already shown by supporters of the electrostatic nature of gravita-

* *Phil. Mag.* p. 571 (March 1936).

tion, would also account for the reciprocal perturbations in the planetary movements. An electrostatic action might account for an increase in the curvature of the comparatively fixed shape of the orbits as they are at present, while a very remote origin of the curvature seems due to a factor whose action is old as the motion, not added to nor apart from it, which, as already mentioned, can be identified with a characteristic of our space.

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3rd April, 1936.

LXVI. *The Magneto-Optical Dispersion of Organic Liquids in the Ultra-Violet Region of the Spectrum.*—Part IX. *The Magneto-Optical Dispersion of Formic Acid, Methyl Formate, and Iso-Propyl Formate.* By BERYL P. M. WALTERS, Ph.D., and Prof. E. J. EVANS, D.Sc., Physics Department, University College of Swansea *.

Introduction.

THE experimental methods employed in the investigation of the magneto-optical rotations and the refractive indices of the three organic liquids have been already described in detail †. The results have been examined in relation to Larmor's theory ‡ of magnetic rotation. According to this theory, the value of Verdet's constant δ for a wave-length λ is given by the expression

$$\delta = - \frac{e}{2mc^2} \cdot \lambda \cdot \frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the refractive index, e/m is the ratio of the charge to the mass of the resonators, and c the velocity of light.

In the above expression the charge e is measured in electrostatic units and the magnetic field in electro-

* Communicated by Prof. E. J. Evans.

† Stephens and Evans, *Phil. Mag.* x. p. 759 (1930).

‡ 'Æther and Matter,' Appendix F, p. 352.

magnetic units. If the ordinary dispersion of each is represented by an equation of the type

$$n^2-1=b_0+\frac{b_1}{\lambda^2-\lambda_1^2}+\frac{b_2}{\lambda^2-\lambda_2^2}+\dots \quad (2)$$

EXPERIMENTAL RESULTS.

Ordinary Dispersion.

TABLE I. (A).

Visual Determinations.

Wave-length in microns.	Refractive indices.		
	Formic acid at 12.6° C.	Methyl formate at 7.4° C.	Iso-propyl formate at 11.9° C.
·6678	1.3717 ₆	1.3474 ₉	1.3698 ₄
·5876	1.3743 ₆	1.3495 ₇	1.3720 ₁
·5016	1.3784 ₁	1.3531 ₅	1.3756 ₁
·4922	1.3787 ₀	1.3533 ₁	1.3762 ₀
·4713	1.3804 ₂	1.3549 ₆	1.3774 ₁
·4472	1.3823 ₈	1.3568 ₂	1.3791 ₈

and the magneto-optical dispersion over the range of spectrum investigated is controlled by one absorption band in the ultra-violet, it can be shown that

$$\phi=n\delta\lambda^2=K\left(\frac{\lambda^2}{\lambda^2-\lambda_1^2}\right)^2, \quad \dots \quad (3)$$

where K is a constant and λ_1 the wave-length of the absorption band. In addition, the value of $\frac{e}{m}$ deduced from the above three equations is given by the expression

$$\frac{2Kc^2}{b_1}.$$

Each of the three liquids employed in this investigation was subjected to a process of fractional distillation before use, and the fraction which distilled over near the accepted boiling-point was employed in the determinations of the refractive indices. In the case of formic acid the fraction which distilled over at the accepted

boiling-point was further cooled down to 8.4°C . and the crystals collected. These crystals melted at a higher

TABLE I. (B).
Photographic determinations.

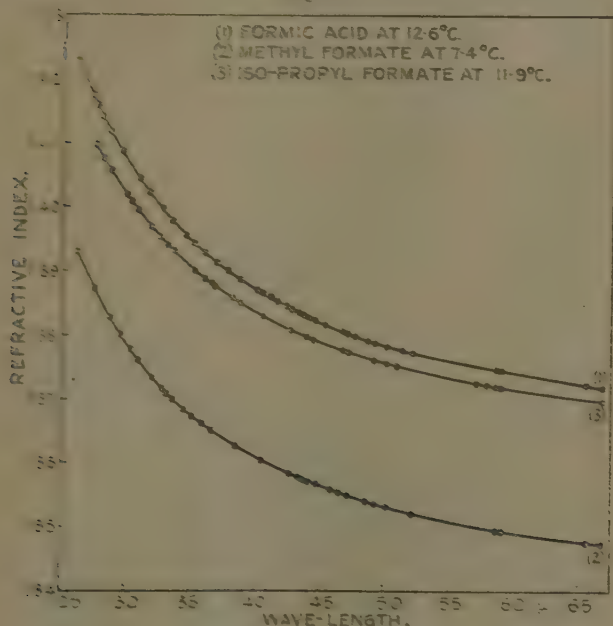
Formic acid at 12.6°C .		Methyl formate at 7.4°C .		Iso-propyl formate at 11.9°C .	
Wave-length in microns.	Refrac- tive index.	Wave-length in microns.	Refrac- tive index.	Wave-length in microns.	Refrac- tive index
·5218	1.3769 ₉	·5218	1.3522 ₇	·5782	1.3723 ₆
·5145	1.3776 ₅	·4651	1.3553 ₆	·5732	1.3725 ₈
·4768	1.3799 ₀	·4587	1.3560 ₄	·5106	1.3751 ₅
·4697	1.3806 ₀	·4415	1.3573 ₁	·4705	1.3774 ₅
·4675	1.3806 ₇	·4378	1.3576 ₃	·4416	1.3796 ₈
·4537	1.3818 ₁	·4265	1.3583 ₉	·4275	1.3807 ₅
·4490	1.3822 ₄	·4063	1.3604 ₀	·4063	1.3828 ₉
·4415	1.3828 ₅	·3862	1.3625 ₄	·3881	1.3849 ₀
·4378	1.3832 ₁	·3680	1.3650 ₄	·3825	1.3856 ₁
·4275	1.3842 ₀	·3600	1.3662 ₀	·3689	1.3875 ₃
·4254	1.3843 ₈	·3520	1.3670 ₆	·3656	1.3880 ₄
·4178	1.3852 ₄	·3450	1.3682 ₂	·3600	1.3888 ₅
·4123	1.3858 ₅	·3382	1.3699 ₆	·3535	1.3899 ₀
·4064	1.3863 ₈	·3317	1.3708 ₀	·3365	1.3931 ₀
·4022	1.3869 ₆	·3290	1.3714 ₄	·3317	1.3939 ₅
·3882	1.3886 ₉	·3208	1.3732 ₉	·3260	1.3953 ₂
·3804	1.3898 ₀	·3108	1.3759 ₇	·3194	1.3967 ₃
·3720	1.3914 ₃	·3036	1.3777 ₄	·3112	1.3996 ₃
·3610	1.3929 ₈	·2961	1.3801 ₅	·3036	1.4009 ₃
·3531	1.3943 ₀	·2883	1.3825 ₅	·3012	1.4016 ₂
·3470	1.3955 ₇	·2766	1.3871 ₇	·2997	1.4019 ₀
·3363	1.3978 ₅	·2622	1.3929 ₇	·2883	1.4055 ₀
·3289	1.3997 ₂			·2825	1.4076 ₂
·3190	1.4024 ₃			·2767	1.4098 ₂
·3097	1.4044 ₈				
·2973	1.4085 ₁				
·2883	1.4116 ₂				
·2815	1.4141 ₄				
·2775	1.4158 ₇				
·2766	1.4161 ₃				
·2634	1.4225 ₀				
·2625	1.4228 ₀				

temperature, and the liquid obtained in this way was employed in the determination of the refractive indices.

The refractive indices given in Tables I. (A) and I. (B) were determined at temperatures in the neighbourhood of 20°C ., and were corrected to the temperatures at

which the magneto-optical rotations were measured by making use of the known values of the temperature coefficients of the three liquids. It was found that the refractive indices of formic acid, methyl formate, and, iso-propyl formate diminished by $\cdot 000 \pm_0$, $\cdot 000 \pm_2$, $\cdot 00 \pm_2$ respectively per degree C. rise of temperature. The refractive indices of the three liquids for various wave-lengths are plotted in fig. 1.

Fig. 1.



Magneto-Optical Dispersion.

Formic Acid.

The sample of formic acid was fractionated at a pressure of 767.5 mm., and the portion distilling over between 100.7° C. and 100.8° C. was retained. This fraction was then cooled down to 8.4° C., and the crystals of formic acid so formed were collected. The crystals were allowed to melt, and the results obtained from this sample are given in Table II, (A) and plotted in fig. 2.

Fig. 2.

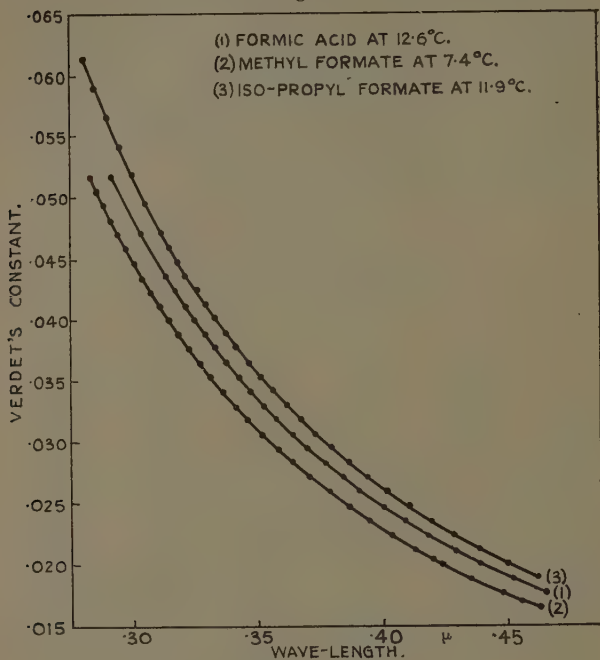


TABLE II. (A).
Verdet's Constant of Formic Acid.
(Temperature 12.6° C.)

Wave-length in microns.	Verdet's constant in min./cm. gauss.	Wave-length in microns.	Verdet's constant in min./cm. gauss.
·4648	·0176 ₄	·3525	·0329 ₅
·4521	·0188 ₃	·3472	·0341 ₂
·4398	·0199 ₈	·3422	·0352 ₉
·4287	·0211 ₃	·3375	·0364 ₇
·4184	·0223 ₄	·3332	·0376 ₅
·4089	·0235 ₂	·3293	·0388 ₂
·3999	·0246 ₉	·3253	·0400 ₀
·3917	·0258 ₇	·3210	·0411 ₇
·3840	·0270 ₆	·3172	·0423 ₅
·3770	·0282 ₃	·3138	·0435 ₂
·3703	·0294 ₁	·3043	·0470 ₄
·3640	·0305 ₉	·2919	·0517 ₄
·3580	·0317 ₇		

Table II. (B) gives a series of values of the refractive index n and Verdet's constant δ for the given wave-lengths. These values were obtained from fig. 1 and Table II. (A) respectively. It was found that the experimental results could be represented by a formula of the type

$$\phi = n\delta\lambda^2 = K \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2,$$

and from several pairs of values obtained from Table II. (B) λ_1 and K were calculated.

TABLE II. (B).

	λ (microns).	δ (min./cm. gauss).	n .
(A)	·4398	·0199 ₈	1·3830 ₁
(B)	·3999	·0246 ₉	1·3872 ₄
(C)	·3472	·0341 ₃	1·3955 ₃
(D)	·3172	·0423 ₅	1·4028 ₃

Substitution in the above equation gave the following results :—

From (A) and (B) $\lambda_1 = \cdot 1030 \mu$ and $K = 4\cdot 775_2 \times 10^{-3}$.

„ (B) and (C) $\lambda_1 = \cdot 1029 \mu$ and $K = 4\cdot 777_7 \times 10^{-3}$.

„ (A) and (D) $\lambda_1 = \cdot 1037 \mu$ and $K = 4\cdot 767_0 \times 10^{-3}$.

„ (C) and (A) $\lambda_1 = \cdot 1031 \mu$ and $K = 4\cdot 773_6 \times 10^{-3}$.

The mean values of λ_1 and K are $\cdot 1032 \mu$ and $4\cdot 77_3 \times 10^{-3}$ respectively, and the equation representing the magneto-optical rotation of formic acid for the range of spectrum investigated, at a temperature of $12\cdot 6^\circ \text{C}$., is

$$n\delta = 4\cdot 77_3 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (\cdot 1032)^2\}^2}.$$

Using this equation, the values of Verdet's constant were calculated for wave-lengths at which experimental determinations had been made, and a comparison between the observed and calculated values is given in Table II. (C).

The equation was also employed to calculate Verdet's constant for sodium light; the value obtained being $\cdot 0106_4$ at $12\cdot 6^\circ \text{C}$.

The mean of the last four values of the molecular rotation of formic acid as given by Perkin * is 1.682. Correcting for the variation of relative density of the acid with temperature, the specific rotation is found to be .809 at 12.6° C., and Verdet's constant (taking its value for water as .0131), is found to be .0106₀.

TABLE II. (C).

λ (microns).	δ (observed).	δ (calculated).
.46480176 ₄	.0177 ₀
.45210188 ₃	.0188 ₁
.42870211 ₆	.0211 ₅
.40890235 ₂	.0235 ₀
.39170258 ₇	.0258 ₈
.37700282 ₃	.0282 ₃
.36400305 ₉	.0305 ₉
.35250329 ₅	.0329 ₆
.34220352 ₉	.0353 ₂
.33320376 ₅	.0376 ₂
.32100411 ₇	.0411 ₀
.31720423 ₅	.0423 ₀
.29190517 ₄	.0518 ₇

TABLE II. (D).

λ (microns).	Magnetic rotary power relative to that at .5461 μ .	
	Lowry and Dickson.	Present results.
.6708647	.648
.6438708	.707
.5893852	.851
.5086	1.164	1.164
.4800	1.322	1.320
.4359	1.635	1.630

A comparison of Lowry and Dickson's † results with the values of the magnetic rotary power relative to that at .5461 μ calculated from the above equation is given in Table II. (D).

* Perkin, Journ. Chem. Soc. vol. i. p. 480 (1884).

† Lowry and Dickson, Int. Crit. Tables, vol. vi. p. 434.

Methyl Formate.

The specimen of methyl formate employed in the measurements of the magneto-optical rotations distilled over between 31.5° C. and 31.6° C. at a pressure of 751 mm. The experimental results are given in Table III. (A) and fig. 2.

TABLE III. (A).
Verdet's Constant of Methyl Formate.
(Temperature = 7.4° C.)

Wave-length in microns.	Verdet's constant in min./cm. gauss.	Wave-length in microns.	Verdet's constant in min./cm. gauss.
·4630	·0164 ₄	·3361	·0340 ₇
·4551	·0170 ₄	·3312	·0352 ₃
·4487	·0176 ₁	·3266	·0364 ₃
·4356	·0187 ₉	·3224	·0375 ₉
·4239	·0199 ₇	·3185	·0387 ₆
·4202	·0203 ₆	·3147	·0399 ₃
·4133	·0211 ₄	·3110	·0411 ₁
·4034	·0223 ₂	·3074	·0422 ₉
·3943	·0235 ₀	·3039	·0434 ₆
·3861	·0246 ₇	·3006	·0446 ₃
·3782	·0258 ₄	·2975	·0458 ₁
·3708	·0270 ₂	·2944	·0469 ₈
·3639	·0282 ₀	·2915	·0481 ₅
·3576	·0293 ₇	·2888	·0493 ₃
·3518	·0305 ₄	·2861	·0505 ₁
·3463	·0317 ₃	·2837	·0516 ₈
·3411	·0328 ₀		

TABLE III. (B).

	λ (microns).	δ (min./cm. gauss).	n .
(A)	·4133	·0211 ₄	1.3595 ₉
(B)	·3708	·0270 ₂	1.3646 ₀
(C)	·3224	·0375 ₉	1.3729 ₇
(D)	·2888	·0493 ₃	1.3824 ₄

From (A) and (D) $\lambda_1 = .1041 \mu$ and $K = 4.307_9 \times 10^{-3}$.
 „ (B) and (C) $\lambda_1 = .1045 \mu$ and $K = 4.295_5 \times 10^{-3}$.
 „ (C) and (D) $\lambda_1 = .1044 \mu$ and $K = 4.298_4 \times 10^{-3}$.
 „ (B) and (D) $\lambda_1 = .1045 \lambda$ and $K = 4.297_6 \times 10^{-3}$.

In Table III. (B) values of Verdet's constant and the refractive indices corresponding to certain wave-lengths are given. These values were used to calculate the constants of the magneto-optical dispersion equation for methyl formate.

The mean values of λ_1 and K are $\cdot 1044\mu$ and $4\cdot 29_9 \times 10^{-3}$ respectively, and the equation representing the magneto-optical dispersion of methyl formate at $7\cdot 4^\circ$ C. over the region of spectrum investigated is

$$n\delta = 4\cdot 29_9 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (\cdot 1044)^2\}^2}.$$

TABLE III. (C).

λ (microns).	δ (observed).	δ (calculated).
$\cdot 4630$	$\cdot 0164_4$	$\cdot 0164_2$
$\cdot 4551$	$\cdot 0170_4$	$\cdot 0170_6$
$\cdot 4356$	$\cdot 0187_9$	$\cdot 0188_1$
$\cdot 4202$	$\cdot 0203_3$	$\cdot 0203_4$
$\cdot 3943$	$\cdot 0235_0$	$\cdot 0234_9$
$\cdot 3782$	$\cdot 0258_4$	$\cdot 0258_9$
$\cdot 3576$	$\cdot 0293_7$	$\cdot 0294_0$
$\cdot 3411$	$\cdot 0328_9$	$\cdot 0328_6$
$\cdot 3266$	$\cdot 0364_3$	$\cdot 0364_5$
$\cdot 3147$	$\cdot 0399_3$	$\cdot 0399_3$
$\cdot 3006$	$\cdot 0446_3$	$\cdot 0446_2$
$\cdot 2944$	$\cdot 0469_8$	$\cdot 0469_9$
$\cdot 2861$	$\cdot 0505_1$	$\cdot 0505_1$
$\cdot 2837$	$\cdot 0516_8$	$\cdot 0516_0$

This equation was used to calculate δ for some wave-lengths at which experimental determinations had been made, the values of n being read off from fig. 1. A comparison of the observed and calculated values is given in Table III. (C).

The value of Verdet's constant for sodium light was calculated from the equation, and was found to be $\cdot 0097_8$.

The density of methyl formate relative to water at $7\cdot 4^\circ$ C. as determined by a specific gravity bottle was $0\cdot 9922$, and the calculated value of the molecular rotation is $2\cdot 508$.

Perkin * found that the molecular rotation of methyl formate is 2.495. It is the mean of three values, of which the highest is 2.510.

Iso-Propyl Formate.

The specimen of iso-propyl formate was fractionated at 770 mm. pressure, the portion which distilled over

TABLE IV. (A).

Verdet's Constant of Iso-Propyl Formate.
(Temperature = 11.9° C.)

Wave-length in microns.	Verdet's constant in min./cm. gauss.	Wave-length in microns.	Verdet's constant in min./cm. gauss.
·4620	·0188 ₅	·3414	·0377 ₀
·4498	·0200 ₂	·3372	·0388 ₈
·4385	·0212 ₀	·3331	·0400 ₄
·4283	·0223 ₇	·3294	·0412 ₀
·4193	·0235 ₄	·3257	·0424 ₀
·4100	·0247 ₂	·3220	·0435 ₇
·4012	·0259 ₀	·3182	·0447 ₅
·3935	·0270 ₈	·3151	·0459 ₂
·3863	·0282 ₆	·3120	·0471 ₀
·3791	·0295 ₃	·3058	·0493 ₆
·3730	·0306 ₃	·3005	·0518 ₁
·3670	·0318 ₀	·2951	·0540 ₆
·3615	·0329 ₇	·2898	·0565 ₃
·3563	·0342 ₅	·2855	·0589 ₀
·3511	·0353 ₃	·2809	·0612 ₄
·3464	·0365 ₂		

at 68.4° C. being retained for use. The experimental results obtained are given in Table IV. (A) and also in fig. 2.

The values of Verdet's constant and the refractive index corresponding to certain wave-lengths, as read off from Table IV. (A) and fig. 1, respectively, are given below in Table IV. (B), and from these results the constants of the magneto-optical dispersion equation were calculated.

* Perkin, Journ. Chem. Soc. vol. i. p. 491 (1884).

TABLE IV. (B).

	λ (microns).	δ mins./cm. gauss.	n .
(A)	·4283	·0223 ₇	1·3806 ₈
(B)	·3863	·0282 ₆	1·3850 ₈
(C)	·3331	·0400 ₄	1·3936 ₀
(D)	·2898	·0565 ₃	1·4048 ₆

From (A) and (B) $\lambda_1 = \cdot 1066 \mu$ and $K = 4.985_4 \times 10^{-3}$.

„ (B) and (D) $\lambda_1 = \cdot 1067 \mu$ and $K = 4.983_8 \times 10^{-3}$.

„ (A) and (D) $\lambda_1 = \cdot 1067 \mu$ and $K = 4.967_7 \times 10^{-3}$.

„ (C) and (D) $\lambda_1 = \cdot 1066 \mu$ and $K = 4.991_1 \times 10^{-3}$.

The mean values of λ_1 and K are $\cdot 1066 \mu$ and 4.982×10^{-3} , respectively, and the equation representing the magneto-optical dispersion of iso-propyl formate at 11.9°C . is thus

$$n\delta = 4.98_2 \times 10^{-8} \frac{\lambda^2}{\{\lambda^2 - (\cdot 1066)^2\}^2}.$$

TABLE IV. (C).

λ (microns).	δ (observed).	δ (calculated).
·4620	·0188 ₅	·0189 ₀
·4498	·0200 ₂	·0200 ₅
·4385	·0212 ₀	·0212 ₁
·4193	·0235 ₄	·0234 ₄
·4100	·0247 ₂	·0246 ₆
·3935	·0270 ₈	·0270 ₈
·3791	·0295 ₂	·0294 ₉
·3615	·0329 ₇	·0329 ₃
·3511	·0353 ₃	·0352 ₈
·3414	·0377 ₀	·0377 ₁
·3294	·0412 ₀	·0411 ₀
·3182	·0447 ₅	·0447 ₀
·3058	·0493 ₆	·0493 ₁
·2951	·0540 ₆	·0540 ₉
·2809	·0612 ₄	·0612 ₀

The accuracy of the representation of the results is shown in Table IV. (C), where a comparison is made of the values of Verdet's constant obtained experimentally and the values calculated from the equation.

The magneto-optical equation was also employed to calculate Verdet's constant for the wave-length of sodium light, and the value obtained was $\cdot 0111_8$ at 11.9°C .

Assuming $\cdot 0131$ as the value of Verdet's constant for water at $\cdot 5893 \mu$, the specific rotation of iso-propyl formate at 11.9°C . relative to that of water is $\cdot 853$. Lowry * obtained $\cdot 847$ as the value for iso-propyl formate at 20°C .

The value of the magnetic rotary power at $\cdot 4359 \mu$ relative to that at $\cdot 5461 \mu$ has been calculated from the equation and compared with Lowry's † value,

	Present result.	Lowry.
$\delta_{\cdot 4359}$		
$\delta_{\cdot 5461}$	1.636	1.638

The Dispersion Equations.

The experimental results have shown that the magneto-optical dispersion of each of the liquids investigated can be explained by the presence of a single absorption band of wave-length λ_1 situated in the Schumann-Lyman region of the spectrum.

The ordinary dispersion of each of the liquids can also be represented within experimental error by the equation

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where λ_1 has the same value as that deduced from the magneto-optical experiments.

The values of the constants b_0 and b_1 can be calculated from two values of the refractive index corresponding to two known wave-lengths.

Formic Acid.

The pairs of values of λ and n used in the calculation of the constants b_0 and b_1 are given in Table V. (A). In that calculation the value of λ_1 was taken to be $\cdot 1032 \mu$.

* Lowry, Journ. Chem. Soc. vol. i. p. 91 (1914).

† Lowry, *loc. cit.*

The mean values of the constants b_1 and b_0 are $\cdot 955_7 \times 10^{-2}$ and $\cdot 8604_5$ respectively; and the ordinary dispersion equation of formic acid at $12\cdot 6^\circ$ C. is

$$n^2 = 1\cdot 8604_5 + \frac{\cdot 955_7 \times 10^{-2}}{\lambda^2 - (\cdot 1032)^2}.$$

TABLE V. (A).

λ (microns).	n .	$b_1 \times 10^2$.	b_0 .
$\cdot 6563$	$1\cdot 3723_9$ }	$\cdot 954_0$	$\cdot 8607_2$
$\cdot 4275$	$1\cdot 3842_6$ }		
$\cdot 5876$	$1\cdot 3743_6$ }	$\cdot 954_5$	$\cdot 8603_4$
$\cdot 3804$	$1\cdot 3898_0$ }		
$\cdot 5016$	$1\cdot 3784_1$ }	$\cdot 960_2$	$\cdot 8601_6$
$\cdot 3610$	$1\cdot 3929_8$ }		
$\cdot 4472$	$1\cdot 3823_8$ }	$\cdot 954_1$	$\cdot 8605_8$
$\cdot 2625$	$1\cdot 4228_0$ }		

In Table V. (B), below, a comparison is given between the observed values and those calculated from the above formula for certain wave-lengths.

TABLE V. (B).

λ (microns).	n (observed).	n (calculated).
$\cdot 5145$	$1\cdot 3776_5$	$1\cdot 3777_0$
$\cdot 4697$	$1\cdot 3806_0$	$1\cdot 3805_7$
$\cdot 4254$	$1\cdot 3843_8$	$1\cdot 3843_9$
$\cdot 3882$	$1\cdot 3886_9$	$1\cdot 3887_4$
$\cdot 3531$	$1\cdot 3943_0$	$1\cdot 3943_4$
$\cdot 3363$	$1\cdot 3978_5$	$1\cdot 3977_7$
$\cdot 3097$	$1\cdot 4044_8$	$1\cdot 4044_8$
$\cdot 2815$	$1\cdot 4141_4$	$1\cdot 4141_4$
$\cdot 2766$	$1\cdot 4161_3$	$1\cdot 4161_9$

Methyl Formate.

The constants b_0 and b_1 of the ordinary dispersion equation were calculated from the following pairs of values of λ and n , and the results are given in Table VI. (A).

TABLE VI. (A).

λ (microns).	n .	$b_1 \times 10^2$.	b_0 .
·6678	1·3474 ₉	·828 ₈	·7967 ₂
·4713	1·3549 ₆		
·5876	1·3495 ₇	·829 ₁	·7965 ₅
·3862	1·3625 ₄		
·5016	1·3531 ₅	·831 ₀	·7964 ₈
·3600	1·3662 ₀		
·4378	1·3576 ₃	·827 ₀	·7973 ₅
·2622	1·3929 ₇		

The mean values of b_1 and b_0 are $\cdot 829_0 \times 10^{-2}$ and $\cdot 7967_8$. Thus the ordinary dispersion equation of methyl formate at $7\cdot 4^\circ$ C. is

$$n^2 = 1\cdot 7967_8 + \frac{\cdot 829 \times 10^{-2}}{\lambda^2 - (\cdot 1044)^2}.$$

From this equation values of n were calculated for several wave-lengths at which experimental values had been found.

A comparison of these two is given in Table VI. (B).

TABLE VI. (B).

λ (microns).	n (observed).	n (calculated).
·5893	1·3495 ₃	1·3496 ₀
·5218	1·3522 ₇	1·3522 ₅
·4861	1·3540 ₃	1·3541 ₀
·4651	1·3553 ₆	1·3553 ₉
·4265	1·3583 ₉	1·3584 ₂
·4063	1·3604 ₀	1·3603 ₇
·3680	1·3650 ₄	1·3650 ₆
·3382	1·3699 ₆	1·3700 ₀
·3108	1·3759 ₇	1·3760 ₃
·3036	1·3777 ₄	1·3776 ₉
·2961	1·3801 ₅	1·3801 ₄
·2883	1·3825 ₅	1·3826 ₁

Iso-Propyl Formate.

The constants of the dispersion equation of iso-propyl formate were calculated using the following pairs of values for λ and n as shown in Table VII. (A).

TABLE VII. (A).

λ (microns).	n .	$b_1 \times 10^2$.	b_0 .
.6678	1.3698 ₄ }	.850 ₁	.8572 ₄
.3881	1.3849 ₀ }		
.5876	1.3720 ₁ }	.851 ₀	.8569 ₆
.3600	1.3888 ₅ }		
.5016	1.3756 ₁ }	.851 ₆	.8568 ₄
.3535	1.3899 ₀ }		
.4472	1.3791 ₈ }	.849 ₂	.8571 ₁
.2883	1.4055 ₂ }		

The mean values of b_1 and b_0 are $.850_5 \times 10^{-2}$ and $.8570_4$.

The ordinary dispersion equation of iso-propyl formate at 11.90° C. is thus

$$n^2 = 1.8570_4 + \frac{.850_5 \times 10^{-2}}{\lambda^2 - (.1066)^2}.$$

In Table VII. (B) is given a comparison between the experimental results at certain wave-lengths and the values calculated from this equation.

TABLE VII. (B).

λ (microns).	n (observed).	n (calculated).
.5782	1.3723 ₅	1.3723 ₆
.5106	1.3751 ₅	1.3751 ₈
.4705	1.3774 ₅	1.3775 ₀
.4416	1.3796 ₈	1.3796 ₂
.4063	1.3828 ₉	1.3828 ₈
.3825	1.3856 ₁	1.3856 ₃
.3656	1.3880 ₄	1.3880 ₂
.3365	1.3931 ₀	1.3931 ₀
.3194	1.3967 ₃	1.3967 ₃
.3112	1.3996 ₃	1.3996 ₇
.3036	1.4009 ₃	1.4008 ₂
.2997	1.4019 ₀	1.4019 ₆
.2825	1.4076 ₂	1.4076 ₀
.2767	1.4098 ₂	1.4098 ₂

The Calculation of $\frac{e}{m}$.

The value of $\frac{e}{m}$ is given by the equation

$$\frac{e}{m} = \frac{2KC^2}{b_1},$$

and can therefore be deduced from the results of the magneto-optical and ordinary dispersion experiments.

The following values were obtained for e/m :—

Formic acid	$\cdot 87_1 \times 10^7$ E.M.U.
Methyl formate	$\cdot 90_5 \times 10^7$ „
Iso-propyl formate ..	$1\cdot 02_2 \times 10^7$ „

DISCUSSION OF RESULTS.

An examination of the observations shows that the magneto-optical dispersion of formic acid, methyl formate, and iso-propyl formate over the range of spectrum investigated can be represented by the equation

$$n\delta = K \frac{\lambda^2}{(\lambda^2 - \lambda_1^2)^2},$$

where n and δ are the values of the refractive index and Verdet's constant for wave-length λ , and λ_1 is the wave-length of the absorption band, which is situated in the Schumann-Lyman region of the spectrum. The values of K and λ_1 vary from liquid to liquid.

Similarly, the refractive indices of the three liquids can be represented within experimental error by the equation

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where λ_1 has the same value as that deduced from the magneto-optical experiments, and the constants b_0 and b_1 depend on the nature of the liquid.

It is of interest to compare the experimental results obtained in this laboratory for formic acid and various formates. These results are collected in Tables VIII. and IX.

TABLE VIII.

Liquid.	Molec. wt.	λ_1 (microns).	$K \times 10^3$.	Temp. °C.
Formic acid, H.COOH	46	·1032	4·77 ₃	12·6
Methyl formate, H.COO.CH_3	60	·1044	4·29 ₉	7·4
Ethyl formate, $\text{H.COO.C}_2\text{H}_5$	74	·1061	4·72	14·8
<i>n</i> -propyl formate, $\text{H.COO.C}_3\text{H}_7$	88	·1077	4·91	20·0
Iso-propyl formate, $\text{H.COO.CH} \begin{array}{l} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	88	·1066	4·98	11·9
Iso-butyl formate, $\text{H.COO.CH}_2\text{CH} \begin{array}{l} \\ \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	102	·1083	5·38	10·7

It is seen from the above Table that the value of λ_1 increases as the molecular weight increases, and also that the value of λ_1 for *n*-propyl formate is not very different from that obtained for iso-propyl formate, which has a different structure. Taking methyl-formate as our starting-point, the value of K also increases with increase of molecular weight.

TABLE IX.

Liquid.	b_0 .	$b_1 \times 10^2$.	$\frac{e}{m} \times 10^{-7}$ E.M.U.	Temp. °C.
Formic acid	·8604 ₅	·955 ₇	·87 ₁	12·6
Methyl formate	·7967 ₈	·829	·90 ₅	7·4
Ethyl formate	·8323	·830	·99 ₆	14·8
<i>n</i> -propyl formate	·8691	·897	·96	20·0
Iso-propyl formate ...	·8570 ₄	·850 ₆	1·02 ₂	11·9
Iso-butyl formate	·9038	·943 ₆	·99 ₃	10·7

A comparison of the formates having the same structure shows that the values of b_0 and b_1 increase with increasing molecular weight. In addition, the values of these two constants diminish in passing from formic acid to methyl formate in the same way as K does (Table VIII.).

In agreement with the results obtained from other magneto-optical investigations it is seen that the value of e/m is considerably lower than the generally accepted value.

LXVII. *Determination of Specific Heat and Thermal Conductivity in a Single Experiment without Thermometry.*
 By W. M. EVANS, M.Sc., *University College of Swansea* *.

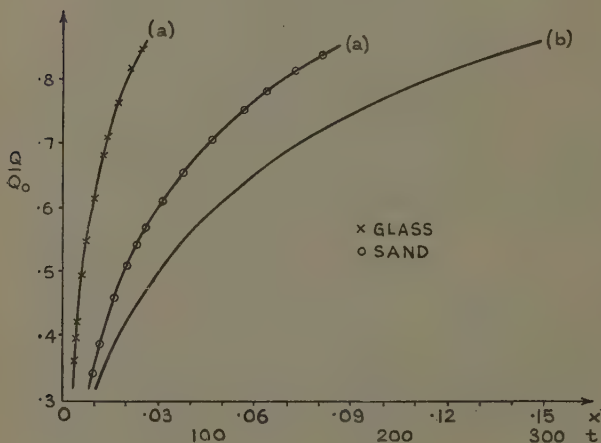
IN the laboratory work carried out by an honours student in physics there is usually a conspicuous lack of experiments illustrating the mathematical methods which he encounters in the theory of heat conduction. The following experiment may therefore be of interest. It may conveniently be substituted for the usual specific heat determination by means of the Joly steam calorimeter, since it includes the whole of that experiment and only differs from it in that the weight of steam condensed is determined, not merely at the end of the condensation, but also at a number of intermediate times. The total weight condensed determines, of course, the specific heat of the substance, and the intermediate weights determine the conductivity. No temperature readings are made, apart from the initial (atmospheric) temperature of the substance.

We take this substance (a poor conductor) in the form of a sphere; if we are using a powder we fill a thin spherical metal shell with it, introducing it through a small hole which we finally close with a thin layer of suitable material. The body is supported so that the steam has ready access to all parts of its surface. During the condensation we do not, of course, measure the weights at given times, but rather the times at which various weights are attained, causing the pointer of the balance to swing over. We attempt no readings during the early stages of the condensation; the process is too rapid. We shall obtain convenient observations over, say, the second half (by weight) of the condensation, and they will be quite sufficient. We apply to all readings the usual correction for radiation etc. and for the difference in the buoyancies of air and steam. Also from all readings we make the usual subtraction of the weight condensed by the pan and support (and the metal shell if we are using one); this is legitimate, for they are good conductors and of small thickness, and will produce practically the whole of their condensation during the early stages of

* Communicated by Prof. E. J. Evans, D.Sc.

the experiment, before we begin making observations. Thus we obtain values of m/m_0 at various values of the time, m being the mass condensed and m_0 its final value (which determines, of course, the specific heat). We regard this ratio as Q/Q_0 , where Q is the heat which has passed into the substance and Q_0 its final value. We count the time t from some arbitrary instant in the experiment, say the turning on of the steam tap. Thus we have the curve of Q/Q_0 against t . The curve (a) in fig. 1 is a typical example. Now if, at some time t_0

Fig. 1.



after our arbitrary zero of time, the surface temperature of the sphere really rose suddenly, through θ_0 from the initial uniform temperature to the upper temperature, at which it remained thereafter, the rise θ in temperature at a distance r from the centre of the sphere, and at time t , would be given by the well-known expression

$$\theta_0 - \theta = \frac{2R\theta_0}{\pi r} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{n} \sin \frac{n\pi r}{R} e^{-n^2\pi^2 x}, \quad \text{for } t > t_0, \quad (1)$$

where

$$x = \frac{K(t-t_0)}{R^2}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

R is the radius of the sphere, and

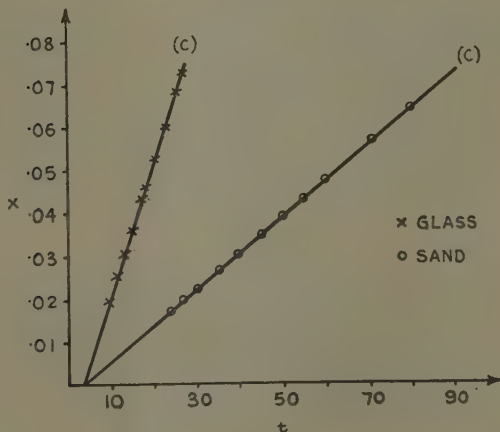
$$K = \frac{\text{conductivity}}{\text{specific heat} \times \text{density}} = \frac{k}{s\rho}.$$

From this by integration we obtain an expression

$$\frac{Q}{Q_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 x}. \quad (3)$$

Confining ourselves to the range of Q/Q_0 observed experimentally, we plot its theoretical value against x by means of (3). Throughout this range the series converges

Fig. 2.



rapidly. We obtain the curve (b) in fig. 1. We now read off corresponding values of x and t for various values of Q/Q_0 , and plot x against t . This is the curve (c) (fig. 2). By equation (2) it is a straight line, giving at once the value of K , whence, since we know the specific heat s from m_0 , we obtain the conductivity k .

The experiment was carried out with a variety of solids and powders, the same curve (b) being used, of course, with all of them. The examples used in the curves (a) and (c) are typical. They gave for glass $s=0.140$, $K=4.88 \times 10^{-3}$, $k=1.72 \times 10^{-3}$; and for sand $s=0.188$, $K=2.5 \times 10^{-3}$, $k=0.83 \times 10^{-3}$. The t_0 given by the line

(c) was 4 seconds * in both cases, counted from the turning on of the steam tap ; its significance will be considered later.

Several sources of error will suggest themselves. It is evident, for instance, that the correction for buoyancy, which assumes a static condition of the steam, will not be accurate. The magnitude of some of these errors will depend on the particular calorimeter used. We shall confine ourselves to those sources of error which are connected with the theory of heat conduction. Firstly, the abrupt change in the surface temperature assumed in (1) and (3) cannot be realised, for it would require heat to be supplied at an infinite rate ; actually the surface temperature must rise as some function of the time. The necessary generalization would present no theoretical difficulty if we knew the function. We can obtain a close approximation by assuming that the whole rise to the upper temperature is accomplished by a time T_0 small compared with any of the t 's in the region of observation. In that case (1), and hence (3), will hold almost exactly in the region of observation on giving t_0 the value

$$T_0 - \int_0^{T_0} \frac{f(T)}{f(T_0)} dT.$$

In other words, for our purpose it is just as if the surface temperature really had changed abruptly, at a t_0 given by this expression †. Such an effect we will call a t_0 effect. Since it does not affect K , it is no source of error at all. Actually, however, even at times not small compared with those observed the surface temperature must differ somewhat from its final value ; for example, there is a fall of temperature through the metal shell if we are using one, and a similar effect due to the layer of water (or more usually the drops of water) on the surface. In the absence of a water layer the effect of the temperature fall in the metal can easily be computed, for we have simply the case of concentric spheres. We find, as we should expect, that it would cause an exceedingly small error in the value found for K (in other words,

* t_0 usually lay between 3 and 10 for the numerous substances tried.

† If, for example, after turning on the tap at an instant taken as the time zero, heat flowed into the sphere at an approximately constant rate during the rise of surface temperature, in which case $f(T)$ would be approximately proportional to \sqrt{T} , t_0 would be approximately $\frac{1}{3} T_0$.

our subtraction of the total mass of water condensed by the shell from all our readings would take adequate account of the effect of the shell). Actually, however, there was water on the surface ; but its amount at various times during the experiment (determined by conducting the experiment with the water-pan removed) was not sufficient to cause more than a small error.

Finally, we may consider the effect of the temperature variations of s and k (the variation of ρ is negligible). Such variations are known to exist, and indeed have played no small part in theoretical physics, but they are consistently neglected in mathematical text-books on heat conduction. Assuming that s and k have small linear variations with temperature throughout the range involved, the differential equation takes on a more complex form, its solutions losing their additive property ; but for given boundary conditions it can be solved to any desired degree of accuracy, given the corresponding solution for s and k constant. For the substances employed it will be sufficient to regard s as constant and consider the variation of k . If it has the value k_0 at the steam temperature, and falls by ck_0 per degree fall in temperature, the calculation, as far as the first power of c , does not give a pure t_0 effect, but tends to it for large values of the time, t_0 being then $3gc\theta_0 R^2/\pi^3 K_0$, where g is a number, about 1 or 2, which can be written in an explicit form if desired. The value of K found from these large t 's is K_0 , the value for the steam temperature, and from it we get k_0 .

I am indebted to Dr. P. M. Davidson for suggesting the experiment and for the mathematics throughout.

LXVIII. *Estimation of Electron Affinities of He, Li, and F.*
By TA-YOU WU, Ph.D., Professor of Physics, National
University of Peking †.

I.

IT is well known that certain elements, especially those having incompletely filled electron shells such as the halogens, have affinity for electrons. The existence of stable negative atomic ions is proved directly

† Communicated by Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

by mass spectrograph analysis. The immediate problem is to determine the binding energy of an electron with a neutral atom. This energy is termed the electron affinity of the atom, and is simply the energy difference between the normal state of the neutral atom and the state of the negative ion. Only when the latter is lower than the former is there a stable negative ion.

It seems that the electron affinity of an atom is not so easily accessible by direct measurement. At present experimental values of electron affinities are available only for a few elements, namely, iodine from the work of Mayer ⁽¹⁾ and oxygen from the work of Lozier ⁽²⁾. Born ⁽³⁾ calculated the electron affinities of such atoms as oxygen, sulphur, and the halogens from considerations based on a cycle of thermal chemical processes. Wave mechanical calculations of the electron affinity have been carried out only for hydrogen ⁽⁴⁾, as such calculations become very laborious as the number of electrons in the system increases. With the statistical potential for a neutral atom Fermi ⁽⁵⁾ obtained the value of 2.2 electron volts for the electron affinity of iodine, as compared with the value 3.1 volts of Mayer. Because of the approximate nature of the statistical potential one would not expect the result to be more than qualitative; and for light atoms the statistical potential cannot very well be applied. This is shown by the values of the electron affinities of F, Cl, Br, and I obtained by solving the Schrödinger equation for an electron in the statistical field of the neutral atom. The equation for the radial part $\psi(r)/r$ of the wave function is

$$\frac{d^2\psi}{dr^2} + \left[E + \frac{2Z}{r} \phi(\gamma r) - \frac{l(l+1)}{r^2} \right] \psi = 0,$$

where E is the energy in units of the ionization potential of hydrogen, r the distance in units of the first Bohr radius of hydrogen, $\gamma = \left(\frac{128Z}{9\pi^2} \right)^{\frac{1}{2}}$, and $\phi(\gamma r)$ the Thomas-

Fermi function. The Wentzel-Brillouin-Kramers method of solving this equation leads to the phase integral of Sommerfeld,

$$\int \sqrt{E + \frac{2Z}{r} \phi(\gamma r) - \frac{(l+\frac{1}{2})^2}{r^2}} dr = (n-l-\frac{1}{2})\pi,$$

for the determination of the eigenvalue E . The values obtained in this way are given in Table I., together with the values obtained by Born ⁽³⁾. It is apparent that these electron affinities obtained by this method can only be regarded as very rough approximations.

Glockler obtained an estimate of the electron affinities of the light atoms in a semi-empirical way ⁽⁶⁾. The electron affinity of an atom of atomic number Z is obtained by extrapolating the ionization potentials of the isoelectronic series of atom and ions with $Z+1$ electrons. Although his results are quite reasonable, it seems that the method is open to one objection, namely, that for a negative ion there is little justification in writing the energy of the electron in the form $\frac{(Z-\sigma)^2}{n^2}$, and the

TABLE I.
Electron Affinities in Electron Volts.

	F.	Cl.	Br.	I.	Z=85.
Born's values	3.75	3.75	3.44	..
Here calculated....	8.1	2.31	4.72	2.72	2.72

"Moseley curve" may show a change in curvature here, so that values for the energies of the negative ions obtained by extrapolation are uncertain.

The object of the present paper is to obtain an estimate of the electron affinities of He in the normal and excited states and of Li in the normal state by the variational method of wave mechanics, and of F by the method of Bacher and Goudsmit ⁽⁷⁾ for the calculation of the energy states of an atom or ion from known data for the higher ions, or *vice versa*. The application of the wave mechanical method is limited to the lighter atoms because of the amount of labour involved as the number of electrons increases, while the method of Bacher and Goudsmit depends on a knowledge of the energy states of the atom in different stages of ionization. The accuracy of the latter method increases with the number of different stages of ions whose energy states are known.

Of the halogens only the energy states of F, F⁺, F⁺⁺, F⁺⁺⁺, F⁺⁺⁺⁺, F⁺⁺⁺⁺⁺, F⁺⁺⁺⁺⁺⁺ are available at present from the beautiful work of Edlén⁽⁸⁾. In the absence of more direct determinations or exact theoretical calculations it is thought worth while to apply these methods to these few atoms.

II.—He, Li.

The energy of a system of N electrons in the field of a nucleus of charge Ze can be obtained by the variational principle of wave mechanics, namely

$$\delta \int \Psi^* H \Psi d\tau = 0,$$

where Ψ is the wave function and H the Hamiltonian of the system. Expressing energy in units of 2R and distance in units of the first hydrogen radius, we have

$$H = - \sum_{i=1}^N \left(\frac{1}{2} \Delta_i + \frac{Z}{r_i} \right) + \sum_{i,j}^N \frac{1}{r_{ij}}.$$

The prime on the second summation sign denotes summation over all pairs of electrons, i. e., $i \neq j$. We shall start with a function Ψ , which is an antisymmetrical combination of one-electron wave functions for the individual electrons, each with an "effective charge" as a parameter. The energy integrals for different electron configurations can be easily evaluated and the energy expressed as a function of Z, and the parameters introduced for the different electrons. The energy is minimized with respect to these parameters, and the minimum value of E is the eigenvalue of the system.

Let us write the radial part $\psi(r)/r$ of the wave functions of 1s, 2s electron in the orthogonal form⁽⁹⁾

$$1s: \psi_1(r) = \sqrt{4\alpha^3} r e^{-\alpha r},$$

$$2s: \psi_2(r) = \sqrt{\frac{12\beta^5}{\alpha^2 - \alpha\beta - \beta^2}} r \left(1 - \frac{\alpha + \beta}{3} r \right) e^{-\beta r}.$$

The energy integrals for the states 1s² 1S, 1s 2s 3S, 2s² 1S, 1s² 2s 2S, 1s 2s² 2S, 1s² 2s² 1S in an atom of nuclear charge Ze are easily obtained:

$$E(1s^2 1S) = \int_0^\infty \left[\left(\frac{d\psi_1}{dr} \right)^2 - \frac{2Z}{r} \psi_1^2 + \psi_1^2 F_0^{11} \right] dr,$$

$$E(1s\ 2s\ ^3S) = \int_0^\infty \left[\frac{1}{2} \left(\frac{d\psi_1}{dr} \right)^2 + \frac{1}{2} \left(\frac{d\psi_2}{dr} \right)^2 - \frac{Z}{r} (\psi_1^2 + \psi_2^2) + \psi_2^2 F_0^{11} - \psi_1 \psi_2 F_0^{12} \right] dr,$$

$$E(1s^2\ 2s\ ^2S) = \int_0^\infty \left[\left(\frac{d\psi_1}{dr} \right)^2 + \frac{1}{2} \left(\frac{d\psi_2}{dr} \right)^2 - \frac{Z}{r} (2\psi_1^2 + \psi_2^2) + \psi_1^2 F_0^{11} + 2\psi_2^2 F_0^{11} - \psi_1 \psi_2 F_0^{12} \right] dr,$$

$$E(1s\ 2s^2\ ^2S) = \int_0^\infty \left[\frac{1}{2} \left(\frac{d\psi_1}{dr} \right)^2 + \left(\frac{d\psi_2}{dr} \right)^2 - \frac{Z}{r} (\psi_1^2 + 2\psi_2^2) + 2\psi_2^2 F_0^{11} + \psi_2^2 F_0^{22} - \psi_1 \psi_2 F_0^{12} \right] dr,$$

$$E(1s^2\ 2s^2\ ^1S) = \int_0^\infty \left[\left(\frac{d\psi_1}{dr} \right)^2 + \left(\frac{d\psi_2}{dr} \right)^2 - \frac{2Z}{r} (\psi_1^2 + \psi_2^2) + \psi_1^2 F_0^{11} + 4\psi_2^2 F_0^{11} + \psi_2^2 F_0^{22} - 2\psi_1 \psi_2 F_0^{12} \right] dr,$$

$$\text{where } F_0^{ij}(r) = \frac{1}{r} \int_0^r \psi_i(\rho) \psi_j d\rho + \int_r^\infty \psi_i(\rho) \psi_j(\rho) \frac{1}{\rho} d\rho.$$

The terms in $\left(\frac{d\psi}{dr} \right)^2$ come from the kinetic energy part of the Hamiltonian ; terms containing Z give the potential energy of the electrons in the field of the nucleus ; terms of the form $\psi_i^2 F_0^{ii}$ are the electrostatic interaction between the electrons ; and terms in $\psi_i \psi_j F_0^{ij}$ are the exchange energy between the electrons in the states i and j . All the integrals can be integrated easily, and the results are given below :

$$\begin{aligned} \int_0^\infty \left(\frac{d\psi_1}{dr} \right)^2 dr &= \alpha^2, & \int_0^\infty \left(\frac{d\psi_2}{dr} \right)^2 dr &= \frac{\beta^2}{3} + \frac{2\beta^4}{\alpha^2 - \alpha\beta + \beta^2}, \\ \int_0^\infty \psi_1^2 \frac{dr}{r} &= \alpha, & \int_0^\infty \psi_2^2 \frac{dr}{r} &= \frac{\beta}{2} - \frac{(\alpha - 2\beta)\beta^2}{2(\alpha^2 - \alpha\beta + \beta^2)}, \\ \int_0^\infty \psi_1^2 F_0^{11} dr &= \frac{5}{8} \alpha, \\ \int_0^\infty \psi_2^2 F_0^{11} dr &= \frac{\beta}{2} - \frac{(\alpha - 2\beta)\beta^2}{2(\alpha^2 - \alpha\beta + \beta^2)} - \frac{(5\alpha + 3\beta)\beta^5}{(\alpha + \beta)^3(\alpha^2 - \alpha\beta + \beta^2)}, \\ \int_0^\infty \psi_2^2 F_0^{22} dr &= \frac{93\alpha^4 - 244\alpha^3\beta + 438\alpha^2\beta^2 - 420\alpha\beta^3 + 245\beta^4}{256(\alpha^2 - \alpha\beta + \beta^2)^2}, \\ \int_0^\infty \psi_1 \psi_2 F_0^{12} dr &= \frac{4\alpha^3\beta^5}{(\alpha + \beta)^5(\alpha^2 - \alpha\beta + \beta^2)}. \end{aligned}$$

It is convenient to introduce a parameter x defined by $\beta = x\alpha$ instead of β . The energy expression becomes then of the form $E = \alpha^2 F(x) - \alpha G(x)$. To obtain the minimum E the writer finds the following process most practicable:—A reasonable value is given to x , and E is calculated for that value of α which makes E minimum for that particular value of x , i. e., $\alpha = G(x)/2F(x)$. Usually one does not have to try more than ten values

TABLE II.

The correction marked * for Li^- is obtained by extrapolation. The value marked ** is the corrected energy value.

$1s^2 2s^2 {}^2S.$	$\text{He}^-.$	$\text{Li}.$	$\text{Be}^+.$	$\text{B}^{++}.$	$\text{He}^- 1s 2s^2 {}^2S.$
α	2.694	3.690	4.693	2.0233
β	0.765	1.365	1.877	.2731
E calc. ..	No minimum.	-7.414	-14.260	-23.353	-2.1528
E obs.	-7.475	-14.321	-23.420
Difference		-0.061	0.061	-0.067
$1s^2 2s^2 {}^1S.$		$\text{Li}^-.$	$\text{Be}.$	$\text{B}^+.$	$\text{C}^{++}.$
α		2.692	3.709	4.710	5.694
β		0.578	1.149	1.695	2.280
E calc.		-7.394	-14.528	-24.188	-36.355
E obs.		-7.494**	-14.664	-24.348	-36.531
Difference		-0.100*	-0.136	-0.160	-0.176

of x to get the minimum E . In Table II. are given the results of such calculations, together with the corresponding observed values ⁽¹⁰⁾.

From the table it is seen that the calculated values differ from the observed values by amounts which are different for different electron configurations and vary with Z for the same electron configuration. The difference between the calculated and the observed energies for $1s^2 2s^2 {}^2S$ is about the same for Li , Be^+ , B^{++} , C^{+++} , while for $1s^2 2s^2 {}^1S$ it increases from Be to C^{++} . The correction

for the state $1s^2 2s^2 {}^1S$ of Li^- can be obtained by extrapolation, and the electron affinity of Li calculated from these corrected energy values come out to be 0.54 volt.

In the case of He the expression for $E(1s^2 2s)$ has no minimum, the energy E becoming smaller for smaller values of $x=\beta/\alpha$ until $x=0$, for which $E=-2.8476$ and is the energy $1s^2 {}^1S$. This means that $1s^2 2s$ is essentially unstable in He. On the other hand, the energy for $1s 2s^2$ has a minimum at $E=-2.153$, while $E(1s 2s {}^3S)=-2.175$. Since the highly excited state $1s 2s^2 {}^2S$ is unobserved in Li, Be^+ , B^{++} , the correction for this state in He^- cannot be determined, but it will lie between -0.01 for $1s 2s {}^3S$ and -0.06 for $1s^2 2s {}^2S$. The corrected value for $1s 2s^2 {}^2S$ of He^- will therefore lie between -2.163 and -2.213 , and will be very close to if not lower than $1s 2s {}^3S=-2.175$. That the negative ion of He has only been infrequently observed in mass-spectrograph ⁽¹¹⁾ is understandable if $1s 2s^2 {}^2S$ is only slightly lower than $1s 2s {}^3S$, for then a helium atom has to be first excited to the state $1s 2s {}^3S$ before a negative ion can be formed. The doubly excited state $2s^2 {}^1S$ has $E=-0.7225$ ⁽¹²⁾. Thus the electron affinity of He in the state $2s^2 {}^1S$ is very large and is of the order of 33.7 volts.

Similar but more tedious calculation for heavier atoms can be made; but as the uncertainty of the result of calculation increases the calculated values will again be only qualitative.

III.—F.

Bacher and Goudsmit ⁽⁷⁾ obtained relations between the energy states of the n -electron spectrum and those of the $(n-1)$ -, $(n-2)$ -, . . . 2-, 1-electron spectra. To obtain the electron affinity of F by this method one has only to obtain the energy of $1s^2 2s^2 2p^6 {}^1S$ in terms of the energy states of the various ions of F. Leaving the two strongly bound $1s$ electrons, we may obtain the relation between the state $2s^2 2p^6 {}^1S$ of the negative ion and the terms of the various spectra F I, F II, F III, F IV, F V, F VI, F VII, after the procedure of Bacher and Goudsmit. Following their notation, we obtain

$$\begin{aligned} s^2 p^6 {}^1S &= (s^2 p^5) 6 {}^2P + (s p^6) 2 {}^2S \\ &\quad - (s^2 p^4) [9 {}^3P + 5 {}^1D + {}^1S] \\ &\quad - (s p^5) [9 {}^3P + 3 {}^1P] - (p^6) {}^1S \end{aligned}$$

Substituting the values in Table III. into the expression (I.) for $s^2 p^6 {}^1S$, one finds the electron affinity $s^2 p^5 {}^2P - s^2 p^6 {}^1S$ to be 43,635 cm.⁻¹, or about 5.45 volts. Apart from the uncertainty of this method of calculation itself, the term value * for $sp^6 {}^3S$ of F I is given by Edlén as an expected value, and is hence not exact. Also the terms ** $p^4 {}^1S$, $p^4 {}^1D$ of F IV and $p^6 {}^1S$ of F II have not been observed. The values given in Table III. are themselves calculated from the states of their respective higher ions by the method of Bacher and Goudsmit, and are therefore of a lower order of approximation than the expression for $s^2 p^6 {}^1S$ of F⁻ would require. However, if one calculates the value of the state $sp^6 {}^2S$ of F I in terms of the states of all the higher ions from the relation

$$\begin{aligned} sp^6 {}^2S = & (sp^5) \left[\frac{9}{2} {}^3P + \frac{3}{2} {}^1P \right] + (p^6) {}^1S \\ & - (sp^4) [6 {}^4P + 3 {}^2P + 5 {}^2D + {}^2S] - (p^5) 6 {}^2P \\ & + (sp^3) \left[\frac{5}{2} {}^5S + \frac{3}{2} {}^3S + \frac{1}{2} {}^5D + \frac{5}{2} {}^1D + \frac{3}{2} {}^3P \right. \\ & \quad \left. + \frac{3}{2} {}^1P \right] + (p^4) [9 {}^3P + 5 {}^1D + {}^1S] \\ & - (sp^2) [6 {}^4P + 3 {}^2P + 5 {}^2D + {}^2S] \\ & \quad - (p^3) [4 {}^4S + 10 {}^2D + 6 {}^2P] \\ & + (sp) \left[\frac{9}{2} {}^3P + \frac{3}{2} {}^1P \right] + (p^2) [9 {}^3P + 5 {}^1D + {}^1S] \\ & - (s) {}^1S - (p) 6 {}^2P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II.) \end{aligned}$$

one gets $E = -5,134,614$ for $sp^6 {}^2S$, and this would lead to the considerably lower value 2.78 volts for the electron affinity. On examining the expressions (I.) and (II.) it is seen that in the calculation of the electron affinity, using for $sp^6 {}^2S$ first Edlén's value and then the calculated value according to (II.), the unknown terms $p^4 {}^1S$, $p^4 {}^1D$ of F IV and $p^6 {}^1S$ of F II appear with equal coefficients but with opposite signs in the two calculations, so that uncertainties in the calculated values of these terms may be removed by taking the average of the two values of the electron affinity, namely $\frac{1}{2}(5.45 + 2.78) = 4.11$ volts. This value seems to be very reasonable when considering the variations of the electron affinities of I, Br, and Cl obtained by Born. Thus, when sufficient data on the spectra of the different ions of an atom are available one can obtain a good estimate of the electron affinity of the neutral atom.

Summary.

The approximate calculation of the electron affinities of the halogens with the Thomas-Fermi potential is shown to be unsatisfactory. The variational method of wave mechanics is applied to the calculation of the electron affinity of Li in the normal state and that of He in the normal and excited states. Corrections to the calculated values of different energy states are made by considering the discrepancy between the calculated and the observed values of similar states of the iso-electronic series of atom and ions. The result is that Li in the normal state has an electron affinity of about 0.54 volt; He in the normal state has no electron affinity; in the $1s\ 2s\ ^3S$ state the electron affinity is probably very small; while in the doubly excited state $2s^2\ ^1S$ it is about 33 volts. The method of Bacher and Goudsmit is applied to the calculation of the electron affinity of F from the data of Edlén. The result is about 4.1 volts.

The paper gives the wave functions for the states $1s^2\ 2s$ of Li, Be^+ , B^{++} ; $1s^2\ 2s^2$ for Li^- , Be, B^+ , C^{++} ; and $1s\ 2s^2$ for He^- . These functions and the Bacher-Goudsmit relations for $s^2\ p^6\ ^1S$ and $sp^6\ ^2S$ may be useful for other purposes.

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December 24, 1935.

LXIX. *On the Persistence of the Sensation of Speech.*By MARIO MARRO, *Dr. Ing.* *

IN a communication to the 'Philosophical Magazine' † Professor Frank Allen remarked that the successful application of the principle of the persistence of vision, or the critical frequency of flicker, to the study of problems of colour vision, suggested the probable value of the analogous principle of the persistence of audition in the solution of problems of the perception of sound. By his important researches on the critical frequency of pulsation of tones he established the precise nature of the function

$$D = \frac{k}{\sqrt{\log N}} + c,$$

where D is the duration of the tone at the critical frequency of pulsation, N the frequency of the tone, and k and c are constants.

The source of the sound was a Stern tonvariator placed inside a box lined with very soft thick felt, through which at a suitable place a hole was cut. The tonvariator was blown by a stream of air to the pressure of which the intensity of the sound is proportional. The periodic interruption of the continuous sound into separate impulses was effected by the rotation of an aluminium disk in which were four symmetrically placed holes of the same size as that in the box. The speed of rotation of the disk was increased until the interrupted sound became just continuous to the ear, and hence the critical frequency of pulsation or flutter of the tone was computed.

From the experimental data Professor Allen also deduced a most important relationship connecting D , the duration of a pulse of sound at the critical frequency of pulsation, P , the blowing pressure of the air in the tonvariator which measures the intensity of the sound, and N , the frequency of vibration of the tone :

$$D = k_1 \log P + c_1,$$

where k_1 and c_1 are constants ‡.

While for light the brightest colours have the smallest values of the duration of the impression at the critical

* Communicated by Prof. Frank Allen, M.A., Ph.D., F.R.S.C.

† Vol. xlvii. p. 50 (1924).

‡ Phil. Mag. xlvii. p. 941 (1924).

frequency of flicker, for sound the opposite is the case, since the greatest intensities have the largest values of the duration of the sound at the critical frequency of pulsation. The mechanisms of the two phenomena are, however, quite different; vision probably results from photoelectric action in the rods and cones of the retina, while in the ear the auditory nerves are excited by mechanical vibrations.

Among physiologists the idea has been strongly held that there existed sounds of interruption or of intermittence, and also tones provoked by phase changes. It was therefore believed that by interrupting u times per second a tone of frequency p there would always be elicited a subjective tone of intermittence with a frequency u . Likewise it was held to be possible to excite a tone of frequency u by varying periodically u times per second the loudness of the sound p , while by changing its phase u times per second there would be obtained sounds of frequencies u and $2u$, which, however, would always be subjective.

The study of these sounds gave rise to the periodic theory of hearing, affirmed especially by Hermann. According to this theory the ear would be able to perceive as a tone any periodic variation whatsoever. But this result would be contradictory to Helmholtz's theory. For a long time this question has been discussed, and, although Hermann persisted in the periodic theory, Abraham, Schultze, and many other men of science have brought forward evidence, derived from repeated experiments, to show that tones of interruption and of change of phase do not exist.

All auditory sensations are excited by vibratory movement, and each sound possesses a pitch which is determined by the number of vibrations exciting it in unit time. But speech is not comparable with music; between speaking and singing wide differences in characteristics exist. Music does not employ all the possible notes but only the well-defined tones and semitones of the diatonic scale. In music notes are sustained for a longer or shorter time, and they have always a duration well appreciated by the ear. In speaking, on the contrary, a given note will last for a very short time, and very often the voice passes from one tone to another touching momentarily all the intermediate pitches. These may differ in frequency by only one or two vibrations per

second, an interval inappreciable to the ear. As the musical intervals of speech may have any values whatever, and the tones are often very fugitive, the ear is unable to catch distinctly the delicate shades of pitch of a spoken phrase. A discriminating and trained ear is able to catch the mean and main pitch of a given utterance, but it cannot specify more exactly its characteristics. Tones change too much and too quickly for the modulating intervals to be precisely detected.

Speech is not a periodic phenomenon of absolutely regular character, and the oscillograms of the phenomena occurring in speech are profoundly different from those of isolated tonal productions. If we record by the oscillograph an uninterrupted series of connected sentences, during which the voice undergoes continuous changes of tone and swift changes of accent and loudness, we shall observe that there is not a succession of steady and uniform periods, but, on the contrary, a continuous transformation of the structure and amplitudes of the periods.

From these considerations I concluded that it was possible to reproduce speech by means of an electric circuit when it was periodically interrupted.

In wire telephonic practice, and very often in wireless telephony, it is necessary to connect alternately with the line, or antenna network, the transmitting apparatus or the receiving one. By proceeding in this way we cannot effect simultaneously both transmission and reception; but if we can devise apparatus of any kind which will permit connexions following each other by time intervals so short that, because of the inertia of the receptors of the ear, the impression of the entrant sound will continue during the period of interruption, it will be possible to obtain simultaneous transmission and reception—that is to say, that telephonic communication between two stations will be carried on in the same way as the conversational exchange between two telephone subscribers living in the same town.

I have carried out the following experiment. On the axle of a small electric motor is fastened a commutator like that of a dynamo. On the revolving surface of the commutator are placed some copper lamellæ and an equal number of insulating lamellæ of the same size, as in fig. 1. Two carbon brushes are supplied, the former of which, A, is continually in contact with the

conducting part of the revolving drum, while the latter, B, alternately touches the conducting and insulating lamellæ, as shown in two positions in fig. 1 (a). During the time intervals, when the brush B touches a copper lamella, the electric circuit of fig. 2 is closed and we can hear the voice speaking into the microphone; but during the time intervals, when the brush B touches an insulating lamella, the electric circuit is opened and no current flows through the earphone. If the commutator rotates with a certain speed we can still catch the speech in a steady manner.

The greater the number of interruptions the less is the loudness of the sound. This phenomenon is particularly conspicuous in the low notes, such as, for example, in the pronunciation of the letter *u* (Italian

Fig. 1.

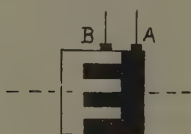


Fig. 1 (a).

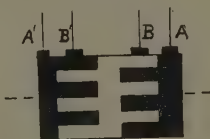
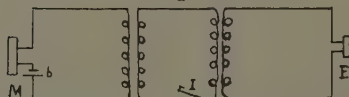


Fig. 2.



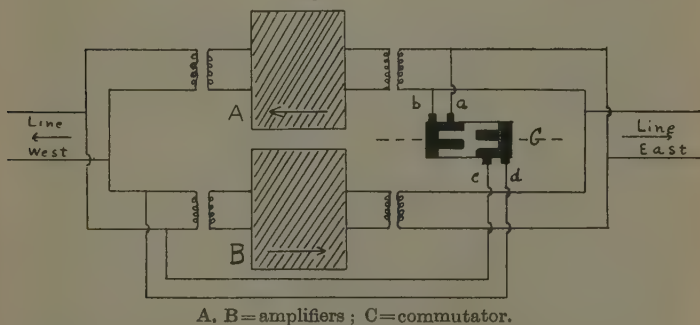
M=microphone; E=earphone; I=interruptor.

muro=wall), the characteristic tone of which has about 225 double vibrations per second; and for certain consonants, such as *r* and *l*, which have several characteristic tones, among which are some indispensable low ones. If we interrupt the speech 250 times per second, because of the persistence of the sound in the ear, the shrill notes will suffer only slight loss, as, for instance, with the vowel *i*, the characteristic tone of which has a frequency of 3600 vibrations. But the tones having frequencies less than 2500 will become diminished by a small amount at each interruption. It will perhaps happen that for a tone of 30 vibrations there will be no sound at all. There are some consonants with such a characteristic tone. This differential effect is probably due to the unequal times required by tones of different frequencies to excite their respective receptors.

For another reason the loudness of tones of all pitches diminishes as the speed of rotation of the commutator becomes smaller, since if the speed is lessened the longer is the duration of the intervals of interruption which are filled only by the persistence of the auditory impressions, whose amplitudes diminish quickly and in the limit become null. The complete auditory impression, being the algebraic sum of the intense sound obtained while the circuit is closed and the weaker one persisting during the time intervals when the circuit is broken, is necessarily diminished.

Fig. 3 represents a unidirectional valve telephone amplifier, inserted in a telephone link circuit, which is alternately connected to and disconnected from the

Fig. 3.



telephone circuit. On an electric motor axle is fastened a drum like that already described. A brush, *a*, presses upon the commutator lamellæ, while another brush, *b*, makes continual contact with the conducting part of the drum. During the time intervals, when the brush *a* is in contact with a copper lamella, the input circuit of amplifier A is short-circuited, and no energy enters from the line into the amplifier. On the contrary, during the same time intervals the input circuit of amplifier B, which acts in the opposite direction to that of amplifier A, is not short-circuited, as brushes *c* and *d* do not close the input circuit of amplifier B. If the arrangement of the copper lamellæ is such that brush *a* touches a copper lamella at the same instant when brush *c* touches the corresponding insulating lamella, the input circuit of amplifier A will then be alternately

short-circuited with respect to the input circuit of amplifier B. Thus the telephone line is alternately connected with the amplifiers A and B. These amplifiers cannot come into oscillation even when their amplifying power is pushed to a high value. A certain lowest frequency of interruption is indispensable to effect a tolerable transmission of voice, below which it becomes gruff and almost unintelligible. There is, however, an optimum frequency of interruption at which the intelligibility is not at all diminished though the quality of the voice becomes slightly hoarse. It is thus demonstrated that reproduction of speech is possible even when it is periodically interrupted.

The condition according to which the voice interruptions are produced is a linear one; thus no condition arises which changes the modulation of the voice by the interruption frequency, since combinational frequencies are produced by the action of two disturbances only when apparatus operates under a non-linear condition. In the present case, when the voice is interrupted by the revolving drum, its reproduction is quite perfect.

The lower threshold of intelligibility—that is, the minimum number of interruptions necessary for a speech pronounced before a microphone to be heard intelligibly—was readily ascertained. Several persons were listening, and during the tests reception of speech ranged from non-intelligibility to intelligibility and conversely. The average of these tests showed that for clear reception of known speech 10 interruptions per second were sufficient, but for unknown speech 15 interruptions were required. These were minimum values, but for clear reproduction of speech with easy and full intelligibility 35 interruptions per second were desirable, with silent intervals of equal duration occurring alternately with intervals of speech.

It is suggestive to notice that in moving pictures at the present time about 25 photograms are projected per second.

The greater the frequency of interruption the better appears to be the perception of continuity of hearing. It is not advisable, however, to exceed a certain number of interruptions, because with higher frequencies the interrupting drum acts as a filter for speech by suppressing the low frequencies and consequently altering the general pitch of the speech tone though not perceptibly its

speech character. In order to recognize a vowel sound two vibrations are sufficient—that is, it is sufficient for the electric circuit to remain closed for a time lasting from $\frac{1}{215}$ th to $\frac{1}{130}$ th of a second. Consequently by interrupting the circuit 35 times per second it will be closed sufficiently long to permit distinct recognition of a vowel sound when pronounced.

The illusion of continuity of hearing in speech may be considered to be created by means of two syllables or speech sounds pronounced successively. If the second syllable has not been articulated there is, of course, no consciousness of its existence. If there is persistence of the first syllable—a posthumous image, so to speak—its psychological effect will merely consist of the protracted perception of a syllable already pronounced. For continuous speech to be established it is necessary that the second syllable should be pronounced. We are consequently led to conclude that, in the considered case, the illusion of continuity is established when both syllables are simultaneously perceived, the first one being retained as an auditory image in the sensorium because of the persistence of the impression.

For the perception of a given syllable a minimum duration is required, which observation shows to be shorter when it is pronounced in a high pitch. When the electric circuit is interrupted with the optimum frequency the voices of women, which are richer in the higher harmonics, are perceived better than the voices of men. Voices of low tone generate wave cycles of smaller frequencies than those of higher pitch. Thus, for the low tones, the cycles endure for a longer time during which, when the commutator closes the electric current, a smaller number of alternations is transmitted, and it will therefore be less easy to understand the syllable. On the contrary, in voices which possess a higher pitch the wave cycles are more numerous, the oscillation cycles become shorter, and the syllables are more intelligible. Observation indicates that for clear perception of a syllable the number of the transmitted vibrations is of greater importance than their duration. When the pitch of the voice is raised to the upper octave by means of a bridge and two rectifiers placed in opposition, voice transmission is improved. Articulation tests also indicate that vowels are perceived better than consonants; but through practice consonants are also well

perceived even when they are sounded in words without meaning. Thus the ear gradually becomes accustomed to recognize the articulation of consonants even under unusual conditions of intonation and in unfamiliar combinations when the electric circuit is periodically interrupted.

There exists, therefore, a definite relation between the continuity of transmitted speech and the frequency of interruption of the electric circuit. The greater the speed of rotation of the drum, and consequently the greater the number of interruptions of the circuit up to the optimum frequency, the better becomes the perceptual continuity of two syllables pronounced successively. On the other hand, the number of interruptions of the circuit will be limited by the time necessary to obtain a clear perception of the harmonic frequencies characteristic of a given syllable. From the observations of the author it appears that a band of interruptions extending from 35 to 50 per second creates the illusion of continuity of speech without prejudice to its characteristic tone.

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LXX. *Relative and Absolute Values of Atomic Levels.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I HOPE that I may be allowed to comment in your pages upon a part of the very interesting paper by Dr. A. E. Sandström, published in your current number (*Phil. Mag.* xxii. p. 171, July 1936) under the above title.

Quoting from Robinson and Clews (*Proc. Roy. Soc.* cxlix. p. 587) Dr. Sandström says :—" In a recent paper Robinson writes that ' it is necessary to retain the crystal values of the X-ray wave-lengths, as the agreement, already imperfect, is made worse if the grating values are taken '." Sandström goes on to say that " This conception cannot be right "—a conclusion in which I cordially concur, and which I was trying to express in the offending passage *and its context*. If this was not sufficiently clear in the original paper the blame must be mine, as, although the paper dealt with the joint work

of Dr. Clews and myself, I was responsible for the form in which it appeared.

Our argument in the Royal Society paper was developed as follows:—It was first pointed out that *if it was desired to retain accepted values of the atomic constants*, it was necessary to adopt the lowest permissible values of e/m_0 and e/h . It was then added that even when this had been done our results could only be kept in agreement with other data by retaining the crystal X-ray wave-lengths; this is the passage quoted by Sandström—in the original it is, by the way, prefaced by the words “Even so,” which were intended to stress the extreme difficulty of making the experiments fit the old values of the constants. The next paragraph of our paper pointed out that a very low value of e/m_0 was unacceptable on other grounds, and the following paragraph gave the latest evidence in favour of the grating wave-lengths. We were, in fact, piling up as dramatically as possible the evidence against the older accepted values.

I will agree that we might with advantage have discussed more fully in our paper the numerical results which could be deduced from our data. I had, however, through the courtesy of its author, already received an advance copy of the typescript of a paper on the same subject by Professor A. E. Ruark. As the matter was fully dealt with in that paper, in the light of the latest value of e , I omitted any further discussion which I might otherwise have included. I did, however, several months ago, summarize most of the evidence (including that of our own experiments) in *favour* of the grating wave-lengths, in the Physical Society’s ‘Reports on Progress in Physics,’ vol. ii. 1935, p. 247. I have also discussed in greater detail the application of our own results in a paper which was just being completed for publication when Dr. Sandström’s article was received.

I am sure that Dr. Sandström is not wilfully misinterpreting my attitude to the experimental facts, but I feel compelled to say that I think he has succeeded in producing a most shocking illustration of the dangers inseparable from the fine old pastime of lifting passages from their context.

Yours faithfully,

H. R. ROBINSON.

Queen Mary College
(University of London).
July 10th, 1936.

LXXI. *Notices respecting New Books.*

Theoretical Astrophysics. By S. ROSSELAND. (International Series of Monographs on Physics.) [Pp. 355.] (Oxford: Clarendon Press, 1936. Price 25s.)

THE investigation of the nature of the stars falls into two clear-cut parts. One may either study the outer envelope, or "atmosphere," of the star, which is alone directly observable, or one may consider what the internal structure of the star can be if it is to have the observed envelope. Professor Rosseland's new treatise deals only with the first problem, which, crudely stated, is as follows:—Given a detailed knowledge of the lines, bands, and "line-profiles" of a stellar spectrum to deduce the state of the material producing them. Obviously, therefore, it is mainly a question of atomic theory, more precisely, of the quantum theory of a gas at high temperature through which flows an intense field of radiation. Thus the first third of the book deals only with quantum mechanics leading up to a discussion of the emission and absorption of radiation in a gas and of the intensity-distribution (the "profile") of energy in a line. Thereafter the author passes on to the stellar spectra themselves. Not only, of course, do these reveal the actual elements present in the stellar atmosphere, but the line-profiles and the total line intensities yield information as to the degree of ionization and temperature of the material and even give the period of rotation of the star as a whole. Zeeman and Stark effects again give valuable information, in the case of the Sun, regarding the magnetic and electric fields present in the solar envelope. Last, but not least, comes the study of "forbidden" lines in the spectra of such exceptional stars as planetary nebulae. The extreme tenuity of the atmospheres of such stars combined with their intense radiation make possible electron transitions forbidden by the ordinary selection rules.

Mention must be made of the delightful style in which the book is written and of the manner in which the subject is presented as a living and developing whole. At every point the reader is shown not only what is known but also the many paths that yet remain to be explored, whilst the necessary mathematical theory is adequately discussed at every step. The book will certainly be of the greatest value both to the astronomer and to the quantum physicist.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

FIG. 2.

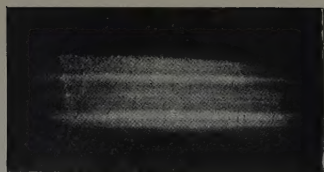


FIG. 3.

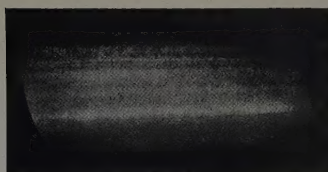


FIG. 4.

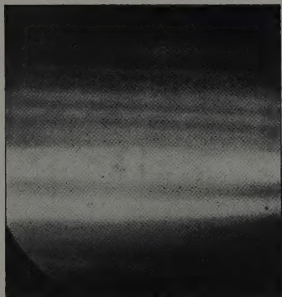


FIG. 5.

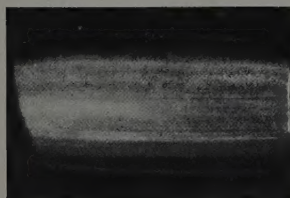


FIG. 7.

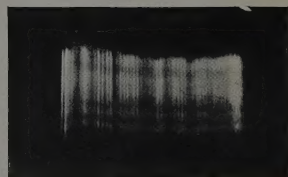


FIG. 8.



FIG. 9.



